

Key Role of Some Specific Occupied Molecular Orbitals of Short Chain n-Alkanes in Their Surface Tension and Reaction Rate Constants with Hydroxyl Radicals: DFT Study

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Abstract

Basing on the DFT calculations we propose the new theoretical model which describes both the surface tension σ of the short chain n-alkanes at their normal boiling points and their reaction rate constants with hydroxyl radicals OH^\bullet (at 297 ± 2 K) on the basis of their molecular orbital electronic characteristics. It has been shown that intermolecular dispersion attraction within the surface liquid monolayer of these compounds, as well as their reaction rate constants k with OH^\bullet radicals are determined by the energies E_{orb} of the specific occupied molecular orbitals which are the same in the determination of both the above physico-chemical characteristics of the studied n-alkanes. The received regression equations confirm the theoretically found dependences between the quantities of σ and k and the module $|E_{orb}|$. For the compounds under study this fact indicates the key role of their electronic structure particularities in determination of both the physical (surface tension) and the chemical (reaction rate constants) properties.

Keywords

Surface Tension, Reaction Rate Constants, n-Alkanes, Hydroxyl Radicals, Dispersion Attraction, Orbital Controlled Interactions, DFT Calculations

1. Introduction

As is known, many physicochemical properties of chemical compounds to a large extent related to some characteristic features of their electronic structure, including, first of all, certain occupied frontier Molecular Orbitals (MOs). On

the one hand, these MOs can determine such physical properties of liquid chemical compounds as surface tension [1] [2], viscosity and electrical conductivity [3], aqueous solubility [4], etc. On the other hand, they are responsible for the wide range of chemical properties: the reaction rate constants [5], enthalpies of formation [6], relative stability of isomers [7], pKa values [8], etc. Here it is important to note, that the above-mentioned occupied MOs are not necessarily the highest occupied MOs (HOMOs) of the compounds under study. So, in the works [1] [2] [8] it was shown that the occupied MOs which are responsible for the studied physicochemical properties can be HOMO-1, HOMO-2, etc.

In particular, in our previous work [1] it has been shown that the surface tension σ of the near-boiling liquids whose molecules possess $\pi\sigma^*$ -hyperconjugated electronic structures is determined by certain occupied MOs which explicitly describe this $\pi\sigma^*$ -hyperconjugation of the methyl groups of each molecule with its π -electron system. As in the present work we study the surface tension of boiling n-alkanes, one can assume that this quantity may depend on some occupied MO which contains 1 s atomic orbitals (AOs) of all the hydrogen atoms of the studied hydrocarbons. This requirement to the above MO follows from the fact that interaction of neighboring molecules in liquid n-alkanes is being realized via H-H interactions because of carbon atoms' spatial shielding.

The frontier molecular orbitals can also play an important role in the determination of the reaction rate constants for the interaction of structurally related compounds with a common reagent. So, for instance, it in the work [5] the energies of these MOs of various organic compounds fit very well for the quantitative description of the reaction rate constants for their interaction with the free radicals O_2^{\bullet} and HO_2^{\bullet} . At the same time there is a great number of the experimental data, describing the reaction rate constants of n-alkanes with free hydroxyl radicals HO^{\bullet} . It can be assumed that in the case of the interaction "hydrocarbon-OH radical" there is also a certain occupied molecular orbital, which is responsible for this process.

In this connection the main goals of the present work are twofold:

- 1) to understand the mechanism of formation of monomolecular surface layers for the liquids under consideration and to find an equation connecting the surface tension of n-alkanes at their normal boiling points with calculated molecular electronic structure parameters;
- 2) to clarify the transition state for the interaction "hydrocarbon-OH radical" and to determine the specific molecular orbitals of n-alkanes which play the crucial role in this reaction. Then, based on this knowledge, to establish a quantitative relationship between properties of these specific MOs and the reaction rate constants for the above interaction.

2. Theory

2.1. Construction of Surface Layers and Surface Tension of Near-Boiling n-Alkanes

In our previous work [1] it has been shown that the surface tension σ of the

near-boiling liquids whose molecules possess $\pi\sigma^*$ -hyperconjugated electronic structures is determined by the formation of some supramolecular $\pi\sigma^*$ -hyperconjugated electronic film-like system including all the molecules entering their surface monomolecular layers. For such liquids the values of σ can be received from the following equation:

$$\sigma = \chi |E_{orb}| NV^{-2/3} (1 - T/T_c), \quad (1)$$

where V is the molar volume of the liquid taken at a certain absolute temperature T , close to or equal to its normal boiling point, T_c is its critical temperature, and N is the total number of molecular centers which form one-particle $\pi\sigma^*$ -hyperconjugated electronic system. The quantity $|E_{orb}|$ in Equation (1) is the absolute value of the energy of the molecular orbital (MO) responsible for $\pi\sigma^*$ -hyperconjugation. The constant χ (equals to $2.6805 \times 10^{-3} \text{ mol}^{1/3}$ at the pressure $P = 0.1 \text{ MPa}$) does not depend on the nature of the considered liquids.

The choice of a monomolecular layer as a system whose properties determine the surface tension [1] was based on the fact that for near-boiling liquids the surface boundary layers practically do not interact with the molecules from their volume phases. The absence of such an interaction follows from a significant increase in the average distances between the liquid layers, especially at temperatures T close to the boiling points. It should be noted that at T , significantly lower than the boiling point T_b , the surface tension becomes depending on the interaction of the upper surface layer with the nearest one [2].

Since in the present work we study the surface tension of boiling n-alkanes, one can expect that this quantity is also determined by the inter-molecular attraction within monomolecular surface layer. It is also clear that the electronic nature of this formation can differ from that of the above considered near-boiling liquids with molecular $\pi\sigma^*$ -hyperconjugation for which the values of σ were found to be related to their molecular electronic structure.

Earlier it was shown that σ for different liquids (including the boiling ones) can be described by the following equation (see Equation (5) from [1]):

$$\sigma = \varepsilon_0 (1 - T/T_c) n \quad (2)$$

where n is the number of surface liquid molecules that must be removed from their equilibrium positions in order to increase the initial liquid surface by one-unit area. Further, ε_0 is the absolute value of the average one-particle zero-point binding energy describing any separate molecule of the surface liquid layer at $T = 0 \text{ K}$.

It was also shown [1] that the quantity ε_0 is proportional to the absolute value of the one-particle energy of intermolecular dispersion attraction $|E_d|$:

$$\varepsilon_0 = \kappa |E_d| = \varphi N |E_{orb}|. \quad (3)$$

In its turn, $|E_d|$ is directly proportional [9] to the value of $|E_{orb}|$, where E_{orb} is the energy of those MOs which contribute essentially to dispersion attraction. Usually, the given MOs are the HOMOs or the nearest to the HOMOs occupied molecular orbitals [9]. The coefficients of proportionality κ and φ are supposed

to be constant for different liquids [1], and N is the number of the atoms, whose atomic orbitals enter the above MOs with great coefficients.

Before determining the number n in Equation (2) one should consider some structural features of the surface monolayer of liquid n-alkanes. So, for the wide temperature range of liquid n-alkanes it has been shown experimentally [10], [11] and theoretically [12] that the hydrocarbon chains of their molecules, forming this monolayer, are oriented normal to its plane. Such an orientation of the hydrocarbon chains of n-alkanes results in the following effects. Firstly, the layer has a certain thickness, and secondly, the terminal one-particle methyl groups are on the opposite sides of the monolayer. Thus, the dispersion attraction, which is responsible for the stability of the considered surface monolayer, acts mainly within its volume (but not on its surfaces as it was described for organic molecules in [1]).

Let us consider in more detail the formation of a new unit surface area of a liquid n-alkane. It can be modeled by removing a straight circular cylinder with a unit base area from its surface layer. The choice of just such a cylinder as the volume to be removed is due to the requirement of a minimum of the total energy necessary to overcome the dispersion attraction between the molecules from its side surface and the neighboring molecules outside the cylinder.

The energy of this intermolecular attraction is proportional to the number of molecules situated on the cylinder's side surface, and therefore, to its side surface area. Therefore, a cylinder with the smallest side surface, namely a straight circular cylinder, will correspond to the minimal total attractive energy.

Since the base of the cylinder is a unit area circle, its radius r is equal to one $\pi^{-1/2}$. Then the value of its side surface area S equals to $2\pi rL$ or $2\pi^{1/2}L$ (where L is the thickness of the surface layer). If the area of one n-alkane molecule is s , that the number n in Equation (2) can be determined by the expression:

$$n = S/s = 2\pi^{1/2}Ls^{-1}. \quad (4)$$

Then, using Equations (3) and (4) we can write Equation (2) for surface tension in the form:

$$\sigma = 2\pi^{1/2}\varphi N|E_{orb}|(1 - T_b/T_c)Ls^{-1} \quad (5)$$

Further, it is to be noted that for the molecules of n-alkanes their carbon atoms are spatially shielded by their hydrogen ones. This circumstance means that the dispersion attraction between the molecules within the liquid surface layer arises mainly due to the H...H interactions of the neighboring molecules. Therefore, for the studied n-alkanes the number N in Equation (5) is equal to the total number of the hydrogen atoms entering the above considered occupied MO with its orbital energy E_{orb} . One can expect that the dispersion attraction will be the strongest if this MO has the following properties. Firstly, the number of the hydrogen atoms entering it should be as high as possible. Secondly, all the hydrogen atomic orbitals (AOs) belonging to this MO must have the same sign (+ or -). Thirdly, the given MO has to be either the highest occupied MO

(HOMO) or one of the occupied MOs which is energetically close to the HOMO [9]. In the considered case of n-alkanes, it is this specific molecular orbital (hereinafter we shall denote it as the SMO) that makes the maximum contribution to the dispersive interaction of any pair of neighboring molecules.

2.2. Relationship “n-Alkanes Electronic Structure—Reaction Rate Constants with OH Radicals”

In the second part of the present work we investigate the QSAR between the n-alkanes electronic structure and the rate constants k in their reactions with hydroxyl radicals:



Here R_1 and R_2 are linear alkyl substituents (or one hydrogen atom together with one methyl substituent in the case of ethane).

In order to find the sought expression connecting the rate constants k of the studied reactions (i) with the particularities of n-alkanes' electronic structure we use the Eyring equation from the transition state theory [13]:

$$k = \left[\tau (k_B T) / h \right] \exp(\Delta S / R) \exp(-\Delta H / RT). \quad (6)$$

In Equation (6) k_B and h are the Boltzmann and Planck's constants, respectively, τ is the transmission coefficient of the reactions (i), ΔS and ΔH are, respectively, the entropy and the enthalpy of activation of the transition states for the reactions (i), T is the reaction absolute temperature, and R is the universal gas constant. Further, using the explicit form of ΔH , Equation (6) can be written as:

$$k = \left\{ \left[\tau (k_B T) / h \right] \exp(\Delta S / R) \exp(-P\Delta V / RT) \right\} \exp(-\Delta E / RT) \quad (7)$$

where ΔV is the change of the volume accompanying the formation of the transition state, ΔE is the activation energy, and P is the normal atmospheric pressure ($P = 0.1 \text{ MPa} = \text{const}$).

Moreover, our DFT calculations have shown that the structures of the transition states of all the reactions (i) have some common spatial domain in which hydrogen atom transfer is being realized (see below). Therefore, it is reasonable to assume that the quantities τ , ΔS , and ΔV in Equation (7) are constant for all the studied n-alkanes. Since the absolute temperature of the reactions (i) is also constant ($T = 297 \pm 2 \text{ K}$), so we can present Equation (7) in the following form:

$$k = A \exp(-\Delta E / RT), \quad (8)$$

where A denotes the expression in its curly braces; therefore, A is constant too. In the logarithmic form Equation (8) may be written as:

$$\log k = \log A - \Delta E / RT = C + D\Delta E, \quad (9)$$

where $C = \log A$ and $D = -1/(RT)$ are some constant coefficients.

Further, as the absolute values of the atomic charges on the hydrogen atoms of

the n-alkanes are near to zero, so the reactions (i) belong to the type of orbital-controlled reactions. To estimate the quantity ΔE we have used the expression given by Klopman in his work [14] (see also the work [5]) which describes the energy change of two reactants in the orbital-controlled interactions:

$$\Delta E = \left[2(\beta c_i c_j)^2 \right] / (E_i - E_j). \quad (10)$$

In Equation (10) E_i is the energy of the molecular orbital of the hydroxyl radical, on which its unpaired electron is located, E_j is the energy of the SMO ($E_j = E_{orb}$, see above) for each investigated alkane, c_i and c_j are the LCAO coefficients of the atoms entering the H-atom transfer domain, and β is the resonance integral between the corresponding atomic orbitals. Therefore, one can assume that the value $2(\beta c_i c_j)^2$ in Equation(10) remains constant for all the n-alkanes under study. In this case, Equation (9) for reaction rate constants has the following final form:

$$\log k = C + Z / (E_i - E_{orb}), \quad (11)$$

where the constant $Z = D \cdot \left[2(\beta \cdot c_i c_j)^2 \right]$.

3. Computational Methods

The electronic structures of all the considered n-alkanes in their optimized conformations were calculated by the DFT (B3LYP) method [15] with the 6 - 31 G(d) basis set using the package of quantum chemical programs GAUSSIAN09 [16].

4. Results and Discussion

4.1. Surface Tension of the n-Alkanes

In the present work we have studied the series of the n-alkanes presented in **Table 1**. All these compounds contain linear hydrocarbon chains. The geometry structure calculations show that their optimal conformations have planar hydrocarbon chains for which any four consecutive atoms are in a trans-configuration. Analysis of the occupied MOs of the studied compounds showed that for all the n-alkanes examined, their HOMOs do not satisfy the above criteria for revealing the MOs with the energy E_{orb} . It follows from the fact that the HOMOs are spatially shielded by the hydrogen atoms of the methylene groups, and, therefore, these orbitals cannot contribute to the value of the surface tension (**Figure 1**). The exceptions are ethane and propane where the HOMOs include the methylene hydrogen atoms discussed above, but their AOs enter the HOMOs with different signs (**Figure 1**).

At the same time, for all the studied n-alkanes, we found the such occupied specific MOs denoted earlier as the SMOs which satisfies the above criteria. They include (with the same sign) the 1s-AOs of the hydrogen atoms of all methylene groups, and their energies E_{orb} are close to the energies of the corresponding HOMOs. The corresponding HOMOs and the SMOs for n-propane, n-pentane,

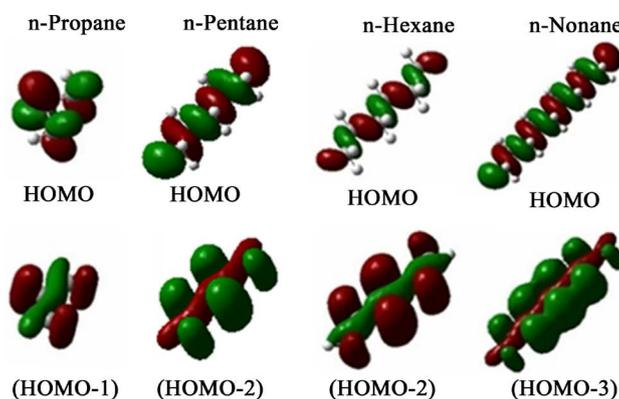


Figure 1. The view of the HOMOs (the upper row) and the SMOs (the lower row) for some of the studied n-alkanes.

n-hexane, and n-nonane are shown in **Figure 1**.

Further, for any investigated n-alkane molecule we consider that the number of its methylene groups (denoted as N_m) is equal to the number of its carbon atoms. It means that its two terminal methyl groups are considered hereafter as the corresponding methylene ones connected with the two end hydrogen atoms belonging to its hydrocarbon chain. Then, the number of the hydrogen atoms N entering the SMO of any n-alkane will be equal to $2N_m$. Besides, since the length of one hydrocarbon chain is proportional to N_m , then the layer thickness L in Equation (5) will be also proportional to N_m due to the normal orientation of the molecules to the two planar sides of the surface monolayer [10] [11] [12]:

$$L = \delta N_m. \quad (12)$$

Further, we assume that the molecules of the surface layer do not leave it for some time, which is large enough to neglect their movement in the normal direction to the two boundary planes of the monolayer. However, these molecules can possess some libration motion changing the angle between their hydrocarbon chains and this normal. The amplitude A of these librations will be also proportional to N_m (if we pass from one n-alkane to another one):

$$A = \lambda N_m. \quad (13)$$

Using the principle of corresponding states and bearing in mind that we deal with the boiling liquids (whose reduced boiling temperatures are very close) we suppose that each of the proportionality coefficients δ and λ in Equations (12), (13) is the same for all the studied n-alkanes. We can also assume that the average one-particle area s in Equation (5) is approximately equal to the area of some rectangle with the sides L and $2A$:

$$s = 2AL = \omega (N_m)^2, \quad (14)$$

where the proportionality coefficient $\omega = 2\delta\lambda$ is constant for any of the studied n-alkanes.

Substituting the defined quantities L , s , and $N = 2N_m$ into Equation (5), we obtain the following expression for the surface tension:

$$\begin{aligned}\sigma &= \left[4\pi^{1/2} \varphi N_m |E_{orb}| (1 - T_b/T_c) \delta N_m \right] \times \left[\omega (N_m)^2 \right]^{-1} \\ &= \xi |E_{orb}| (1 - T_b/T_c) = \xi G\end{aligned}\quad (15)$$

Here the coefficient ξ includes the multiplier $4\pi^{1/2}$ and the constants φ , δ , and τ , and the quantity $G = |E_{orb}|(1 - T_b/T_c)$. Here it is to be noted that the number of methyl groups N_m is not presented in the final Equation (15). Now we have to take into account the influence on σ of the two end hydrogen atoms which belong to the hydrocarbon chain and do not enter the number $2N_m$ (see above). These hydrogen atoms are on the different sides of the surface monolayer, and they enter the corresponding SMOs for all the molecules forming the surface monolayer (**Figure 1**). It means that the interaction between these hydrogen atoms of the neighboring molecules can make some additional contribution to the surface tension. Denoting this contribution as ρ and considering that ρ is a constant for all the investigated n-alkanes, we can rewrite Equation (15) in the form:

$$\sigma = \xi G + \rho. \quad (16)$$

To define the constants ξ and ρ we have studied the set of the boiling short chain n-alkanes presented in **Table 1**. The experimental values of T_b , T_c and σ were taken from [17] [18] [19] [20] [21]. **Table 1** also contains the calculated values of $|E_{orb}|$ which are required for the calculation of $G = |E_{orb}|(1 - T_b/T_c)$. The constants ξ and ρ can be obtained from the linear regression equation obtained by the least square method:

$$\sigma \times 10^3 = 0.0448G + 0.8333. \quad (17)$$

The values of σ calculated by means of Equation (17) are also given in **Table 1** along with the values of σ obtained by the so-called “Leave-one-out” Cross-Validation Scheme (LOOCV). The given statistical method consists in consequent removal

Table 1. The data necessary to estimate the constants ξ and ρ in Equation (16) and the subsequent calculation of σ .

<i>N</i>	Alkane	<i>T</i> (°K)	<i>T</i> _c (°K)	$ E_{orb} $ (kJ/mol)	<i>G</i> (kJ/mol)	$\sigma \times 10^3$ (N/m)		
						Exp.	Calc.	LOOCV
1	Ethane	184.55	305.32	893.58	353.4580	16.31	16.67	16.99
2	Propane	231.11	369.83	873.56	327.6656	15.50	15.51	15.53
3	Butane	272.65	425.12	863.34	309.6393	14.93	14.71	14.67
4	Pentane	309.22	469.70	845.16	288.7624	14.07	13.77	13.72
5	Hexane	341.88	507.60	841.27	274.6572	13.41	13.14	13.12
6	Heptane	371.58	540.20	837.02	261.2699	12.45	12.54	12.57
7	Octane	398.83	568.70	835.47	249.5532	12.09	12.01	11.99
8	Nonane	423.97	594.60	833.73	239.2533	11.53	11.55	11.56
9	Decane	447.30	617.70	833.00	229.7927	10.75	11.13	11.29

*The experimental values of T_b , T_c and σ were taken from [17] [18] [19] [20] [21].

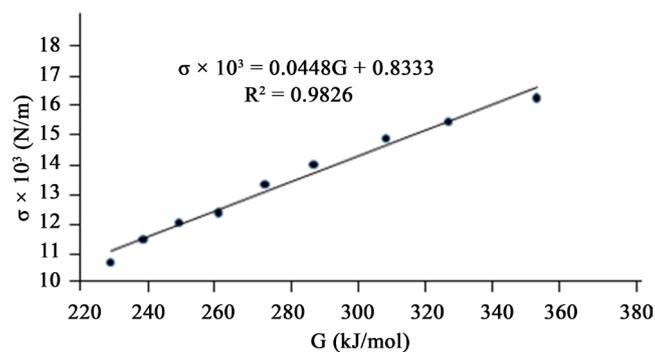


Figure 2. The correlation between the experimental values of σ and the calculated values of G .

of one of the studied compounds from the regression analysis and the following calculation of the predicted quantity for the removed compound. It can be seen that the values of the surface tension in the last two columns of **Table 1** are very close to each other and to the corresponding experimental ones. Note also that the constant $\rho = 0.8333$ in Equation (17) is relatively small in comparison with the amount of $0.0448G$. This fact reflects the small effect of the end hydrogen atoms on σ .

The plot of the correlation between the experimental values of $\sigma \times 10^3$ [$\text{N}\cdot\text{m}^{-1}$] and the calculated parameter G [$\text{kJ}\cdot\text{mol}^{-1}$] is presented in **Figure 2**.

4.2. Rate Constants for the Reactions



First of all, it is to be noted, that our DFT calculations have shown, that, for all the studied n-alkanes, it is these SMOs which determine the values of their surface tension (Section 4.1), are also decisive in their interaction with hydroxyl radicals. So, **Figure 3** demonstrates the interaction of the SMO of n-pentane (**Figure 3(a)**) with the hydroxyl radical HO^\bullet . This interaction generates a transition state characterized by the formation of a three-center C-H-O bond (see **Figure 3(b)**), which can be considered as some spatial domain where the transfer of a hydrogen atom takes place. Redistribution of the electronic density within this C-H-O bond leads to the elongation of the C-H bond and to the simultaneous formation of the new O-H one. Both these processes result in the cleavage of the C-H bond and the appearance of one water molecule and a n-pentyl radical (**Figure 3(c)**).

In Section 4.2 it was found the formulae $\log k = C + Z/(E_i - E_{orb})$, which connects the rate constants k of the above reactions (i) and the energies of the corresponding SMOs. In order to find parameters C , Z , and E_i which are common for all the n-alkanes, we have used the experimental values of k taken from the works [22]-[30] and presented in **Table 2**. The following multiple regression analysis allows one to determine the above parameters. The corresponding numerical values of C , Z , and E_i are equal to 8.1254, 496.25 kJ/mol, and 1003.13 kJ/mol, respectively. The values of $\log k$ calculated by means of Equation (11)

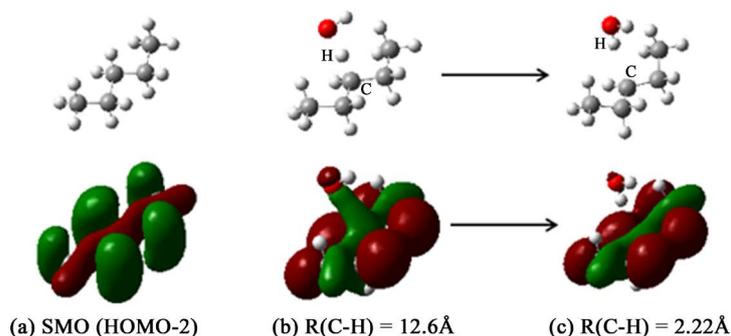


Figure 3. Formation of three-center C-H-O bonding MO between the SMO of n-pentane and the unpaired electron of hydroxyl radical.

Table 2. The data necessary to estimate the constants C , Z , and E_i in Equation (11) and the subsequent calculation of $-\log k$.

N	Alkane	$k_{exp.} \times 10^{12}$ ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	$-\log k_{exp.}$	$ E_{orb} $ ($\text{kJ} \cdot \text{mol}^{-1}$)	$-\log k_{calc.}$
1	Ethane	0.222	12.65	893.58	12.66
2	Propane	1.12	11.95	873.56	11.95
3	Butane	2.10	11.68	863.34	11.68
4	Pentane	5.30	11.28	845.16	11.27
5	Hexane	5.91	11.22	841.27	11.19
6	Heptane	7.26	11.14	837.02	11.11
7	Octane	8.24	11.08	835.47	11.09
8	Nonane	9.36	11.03	833.73	11.05
9	Decane	9.90	11.00	833.00	11.04

with the above parameters are presented in the last column of **Table 2**. As it is seen, the calculated values of $\log k_{calc}$ practically coincide with the corresponding experimental ones. Moreover, these values $\log k_{calc}$ are in a rather good agreement with the latest experimental data [31] [32]. Thus, one can conclude, that Equation (11) describes adequately the relationship between the reaction rate constants k and the energies of the above n-alkanes specific MOs.

5. Conclusions

For the series of short chain n-alkanes we have identified the occupied Specific Molecular Orbitals (SMOs) which play a decisive role in determining their various physical and chemical properties: the surface tension σ near their normal boiling points and the reaction rate constants k with hydroxyl radicals (at 297 ± 2 K). Basing on the theoretical consideration of the intermolecular dispersion attraction in the surface layers and the orbital controlled interactions for the reactions $R_1-(\text{CH}_2)-R_2 + \text{HO}^\bullet = R_1-(\text{C}^\bullet\text{H})-R_2 + \text{H}_2\text{O}$, the two quantitative relationship were received. They connect the energy values $|E_{orb}|$ of these SMOs with the above quantities σ and k . The calculated values of σ and k are in fairly

good agreement with the corresponding experimental data.

Obviously, the results of the present work can be also applied, for example, to cyclo-alkanes and other organic compounds, reacting with free radicals other than OH[•]. It can also be assumed that the revealed role of the SMOs in the aforementioned dispersion attraction may serve for understanding of the nature of evaporation and condensation of the hydrocarbons under consideration. These problems will be considered in our next works.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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