



ENERGY CHARACTERISTICS OF HYDROCARBON - WATER FUEL MIXTURES

G. A. Korablev^[a] and N. V. Khokhriakov^[a]

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The consistent calculations of bond energy in cluster water nanostructures have been performed following the *P*-parameter methodology and quantum-mechanical methods. The formation of high energy bonds in the process of hydrocarbon hydrogen containing fuel preparation has been explained.

* Corresponding Authors

E-Mail: korablevga@mail.ru

[a] Izhevsk State Agricultural Academy, 426069, Russia, Izhevsk, Studencheskaya St., 11,

Introduction

Water plays an ambiguous role in of hydrocarbon fuels of internal combustion engines. On the one hand, simple dilution of petroleum or diesel fuel with water can significantly deteriorate fuel characteristics of the mixture. The water containing fuels¹ can have the potential energy of 1/3 from energy unit of petroleum, and nevertheless the engines produce the same power as with the additional amount of petroleum by the mass equal to the mass of water added.. Specificity of technological processes is ultimately defined by the mechanism of physic-chemical transformations occurring on the atom-molecular level. In this investigation, their possible evaluations are studied based on the concept of spatial energy parameter (*P*-parameter).

Formation of high energy bonds in fuel mixtures

Practical use of hydrogen containing fuel is possible only if a number of conditions are fulfilled:

The introduction of complex additives into the fuel, with alcohols such as ethanol and so-called “hydrogen catalyst” content having the primary meaning.¹ Such additives are mixed following the special technique – first, by separate fractions, and in the end, all the mixture is intensively stirred by a hydraulic cutting pump (hydraulic shears). “Hydrogen catalyst” contributes to active dissociation of water molecules with the formation of hydrogen and oxygen which burn in the engine chamber afterward.

But is not clear how during such a short combustion time of the given amount of mixture introduced into the chamber, water dissociation in this volume and burning of its products

can take place. Moreover, as a result of water dissociation by the reaction $\text{H}_2\text{O}=\text{H}^++\text{OH}^-$ the direct oxygen release is not observed. Obviously, other important mechanisms of physico-chemical transformation of energy are involved. For instance, whose potential energy increases due to the formation of special high energy bonds. It is possible that similar processes take place during the formation of burning mixture. This is aided by the introduction of alcohols (up to 20 %) into the fuel mixture that results in the formation of fullerene, for example, $\text{C}_{60}(\text{OH})_{10}$. High energy bonds formed in the systems $\text{C}_{60}(\text{OH})-n(\text{H}_2\text{O})$ due to the introduction of “hydrogen catalyst” into the mixture.

Similar to ATP hydrolysis which is accompanied by the release of chemical bond energy, the breakage of high energy bonds releases heat in containing fuel when it is burning in the engine chamber. The physico-chemical mechanism of the formation of energy saturated bonds in this system is given below.

Investigation technique

The value of the relative difference of *P*-parameters of interacting atom-components – coefficient of structural interaction α was used as the main numerical characteristic of structural interactions in condensed media:²

$$\alpha = 100 \frac{P_1 - P_2}{(P_1 + P_2) / 2} \quad (1)$$

Applying the reliable experimental data, we obtain the nomogram of the dependence degree of structural interactions upon coefficient α – unified for the wide range of structures. This approach allows evaluating the degree and of structural interactions of phase formation, isomorphism and solubility processes in multiple systems, including molecular ones. In particular, the features of cluster formation in the system $\text{CaSO}_4 - \text{H}_2\text{O}$ have been investigated.³

Table 1. P-parameters of atoms calculated via the electron bond energy

Atom	Valence electrons	W, eV	r_i , Å	q^2 , eV Å	P_0 , eV Å	R, Å	$P_E=P_0/R$, eV
H	1S ¹	13.595	0.5295	14.394	4.7985	0.5295	9.0624
H	1S ¹					0.28	17.137
C	2P ¹	11.792	0.596	35.395	5.8680	0.77	7.6208
C	2P ¹					0.69	8.5043
C	2P ²	11.792	0.596	35.395	10.061	0.77	13.066
C	2S ¹	19.201	0.620	37.240	9.0209	0.77	11.715
C	2S ²				14.524	0.77	18.862
C	2S ² +2P ²				24.585	0.77	31.929
C	1/2(2S ² +2P ²)						15.964
O	2P ¹	17.195	0.4135	71.383	4.663	0.66	9.7979
O	2P ²	17.195	0.4135	71.383	11.858	0.66	17.967
O	2P ²					0.59	20.048
O	2P ⁴	17.195	0.4135	71.383	20.338	0.66	30.815

To evaluate the directness and degree of phase formation processes¹ the following equations are used:

$$\frac{1}{q_2 / r_i} + \frac{1}{W_i / n_i} = \frac{1}{P_E} \quad (21)$$

Initial values of P-parameters:

$$r_E = \frac{1}{r_0 P_0} = \frac{1}{q^2} = \frac{1}{(W r n)_i} \quad (3)$$

$$P_E = \frac{P_0}{r_i} \quad (4)$$

where:

W_i – electron orbital energy;⁴

r_i – orbital radius of i orbital;⁵

$q = Z/n$ – by^{6,7}

n_i – number of electrons in the given orbital,

Z^* and n^* – effective nucleus charge and effective main quantum number.

P_0 is called as spatial energy parameter, and

P_E – effective P-parameter.

The calculation results by equations^{2,3,4} for a number of elements are given in Table 1, from which it is seen that for hydrogen atom the values of P_E – parameters substantially differ at the distance of orbital (r_i) and covalent (R) radii. The hybridization of valence orbitals of carbon atom is evaluated as the averaged value of P-parameters of 2S² and 2P²- orbitals.

Values of P_c -parameter in binary and complex structures:

$$\frac{1}{P_c} = \frac{1}{N_1 P_1} + \frac{1}{N_2 P_2} + \dots \quad (5)$$

where N – number of homogeneous atoms in each subsystem.

The results of such calculations for some systems are given in Table 2.

Bond energy (E) in binary and more complex systems:

$$\frac{1}{E} \approx \frac{1}{P_E} = \frac{1}{P_1(N/k)_1} + \frac{1}{P_2(N/k)_2} \dots \quad (6)$$

where (as applicable to cluster systems) k_1 and k_2 – number of subsystems forming the cluster system; N_1 and N_2 – number of homogeneous clusters.⁷ So for C₆₀(OH)₁₀ $k_1 = 60$, $k_2 = 10$.

Calculations and comparisons

It was assumed that structural-stable water cluster could have the same static number of subsystems (k) as the number of subsystems in the system interacting with it.⁸ For example, the water cluster (H₂O)₁₀ is interacting with fullerene [C₆OH]₁₀.

Similarly with cluster [C₆OH]₁₀ the formation of the cluster [(C₂H₅OH)₆ – H₂O]₁₀ is apparently possible, which corresponds to the system (C₂H₅OH)₆₀ – (H₂O)₁₀. The interaction of water clusters was considered as the interaction of subsystems (H₂O)₆₀ – N(H₂O)₆₀.

Based on such concepts, the bond energies in these systems are calculated by equation 6, the results are given in Table 3. To compare, the calculation data obtained by Khokhriakov N.V. with quantum-chemical techniques¹⁰ are also given.

Both techniques produce consistent values of bond energy (in eV). Besides, the methodology of P-parameter allows explaining why the energy of cluster bonds of water molecules with fullerene C₆₀(OH)₁₀ 2 times exceed the bond energy between the molecules of cluster water (Table 3).

Table 2. Structural P_c-parameters

Radicals, molecules	P ₁ , eV	P ₂ , eV	P ₃ , eV	P ₄ , eV	P _c , eV	Orbitals of oxygen atom
OH	17.967	17.137			8.7712	2P ²
OH	9.7979	9.0624			4.7080	2P ¹
H ₂ O	2 × 17.138	17.967			11.788	2P ²
H ₂ O	2 × 9.0624	17.967			9.0226	2P ²
C ₂ H ₅ OH	2 × 15.964	2 × 9.0624	9.7979	9.0624	3.7622	2P ¹

Table 3. Calculation of bond energy – E, eV

System	C ₆₀ P ₁ /k ₁	(OH) ₁₀ P ₂ /k ₂	(H ₂ O) ₁₀ P ₃ /k ₃	n ₃	P _E , eV From eqn. (6)	E, eV From quantum-mechanical calcn.
C ₆₀ (OH) ₁₀ –N(H ₂ O) ₁₀	15.964/60	8.7712/10	11.788/10	1	0.174	0.176
				2	0.188	0.209
				3	0.193	0.218
				4	0.196	0.212
				5	0.197	0.204
(H ₂ O) ₆₀ –N(H ₂ O) ₆₀	9.0226/60	9.0226/60		n ₂		
				1	0.0768	0.0863
				2	0.1020	0.1032
				3	0.1128	0.1101
				4	0.1203	0.1110
(C ₂ H ₅ OH) ₆₀ –(H ₂ O) ₁₀	3.7622/60	9.0226/10			0.1274	0.115
					0.0586	0.0607
(C ₂ H ₅ OH) ₁₀ –(H ₂ O) ₆₀	3.7622/10	9.0226/60			0.1074	≈ 0.116

Table 4. Spatial-energy interactions in the system H-R, where R= C, (OH), H₂O

System	P ₁ , eV	P ₂ , eV	α=100ΔP/<P>	Spatial bond type
H-C	17.137	15.964	7.09	Covalent
H-OH	9.0624	8.7712	3.27	Orbital
H-H ₂ O	9.0624	9.0226	0.44	Orbital

In accordance with the nomogram, the phase formation of structures can take place only if the relative difference of their P-parameters (α) is under 25-30 %, and the most stable structures are formed when α < 6-7 %.

In Table 4 different values of coefficient α in systems H-C, H-OH and H-H₂O are given, which are within 0.44 – 7.09 (%). The interactions at the distances of covalent radii have been taken into account in the system H-C for carbon and hydrogen atoms, while for other systems – at the distance of orbital radius.

The interaction in system H-C at the distances of covalent radius plays a role of fermentative action, which results in the transition of dimensional characteristics in water molecules from the orbital radius to the covalent one and formation of system C₆₀(OH)₁₀ – N(H₂O)₁₀ with bond energy between the main components 2 times greater than between the water molecules (high energy bonds).

Thus, broad capabilities of water clusters to change their spatial-energy characteristics apparently explain all the diversity of structural properties of water in its different modifications, including the formation of high energy bonds in water containing fuel for internal combustion engines.

Conclusions

Results of bond energy calculations in water cluster nanostructures following the P-parameter methodology agree with quantum-mechanical methods.

Changes which can take place in spatial-energy characteristics of water clusters explain the formation of high energy bonds in the process of hydrocarbon fuel preparation.

The breaking of these bonds with the release of an additional amount of heat energy occurs in the combustion chamber.

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