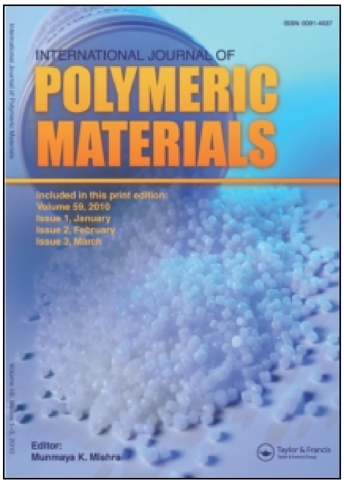

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Quantum-Chemical Calculation of Reactive Fuels as H-Acids

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The theoretical evaluation of acid strength reactive fuels, through quantum-chemical calculation by the method CNDO/2 of the charges on hydrogen atoms, which correlate with the universal index of acidity is presented. Correlations defining relationship of some parameters of combustion with the accounting parameters of acidic strength of the fuels are established to oxygen.

Keywords: Hydrogen atom charges; quantum chemical calculations; CNDO/2 method combustion parameters; reactive fuels

BACKGROUND

The traditional fuels of liquid rockets are classical H-acids (Tab. I). They must satisfy the whole line of demands: they must have high specific impulse, large density, they must be safe in handling, comfortable for storage and besides they must be cheap. Not a single fuel satisfies these demands. That's why one has to make a compromise depending on the priority of this or that demand [1].

Despite the considerable achievements in studying reactive fuels conduct, the role of acidic strength is still vague. The interest to the theoretical evaluation of the acidic strength of reactive fuels such as

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TABLE I Quantum-chemical features of the reactive fuel models

N	*Fuel*	$-E_0$, *kJ/mole*	$-E_{bond}$, *kJ/mole*	*D*, *DB*	$q_{H^+}^{max}$	pK_a [4–8]
1.	H_2	3808	312	0.00	+0.00	+45
2.	N_2H_4	68561	4345	0.28	+0.05	+37
3.	$N_2H_2(CH_3)_2$	114564	10799	3.75	+0.10	+27
4.	NH_3	35998	2237	2.19	+0.07	+33
5.	$C_6H_5NH_2$	153522	18179	1.71	+0.076	+31
6.	C_2H_5OH	97690	–	–	+0.13	+16
7.	H_2O_2	100484	2649	0.27	+0.13	+16
8.	B_2H_6	33198	7365	0.47	+0.22	+4.4

H-acids is a natural result in view of absence of safe experimental methods of the definition of acidity of this class of fuels as they have rather low acidic strength and corresponding indicators are absent. This evaluation can be done if the charges on hydrogen atoms are calculated by quantum chemistry methods that are correlated with quantities of universal index of acidity. This strategy was successfully used for appreciation of a wide class of H-acids.

The aim of this work is the theoretic evaluation of acidic strength of reactive fuels: ethyl alcohol C_2H_5OH, hydrazine N_2H_4, ammonia NH_3, aniline $C_6H_5NH_2$, dimethyl-hydrazine $H_2N_2(CH_3)_2$ and liquid hydrogen H_2, as H-acids (Tab. I) and its correlation with classical parameters of fuels (temperatures of combustion, specific weight of fuels, specific impulse *etc.*). The establishment of correlation between them is important because it will be helpful both in finding new more efficient fuels and developing of the conception of the role of acidic strength in conduct of the above mentioned H-acids, as reactive fuels.

METHODOLOGY

To calculate models of reactive fuels, we used the semi-empirical quantum-chemical CNDO/2 method with Santri-Popla-Seagal parametrization which reproduces the charge characteristics best of all.

To analyze the results of quantum-chemical calculations, we used the following parameters: E_0, the total energy of the system; E_{bon}, the total bond energy; D, the dipole moment; q_A, atomic charges; and some other.

TABLE II Fuel mixtures [1]

N	*Oxidizer*	*Fuel*	φ	*T*, °*K*	M_{burn}	δ	J_{sp}, *s*
1.		NH_3	0.385	4292	19	1.15	306
2.	F_2	N_2H_4	0.500	4555	19	1.30	316
3.		H_2	0.222	3030	8.9	0.32	374
4.	H_2O_2	C_2H_5OH	0.250	2811	23	1.24	245
5.	99.6%	N_2H_4	0.625	2861	19	1.25	263
6.	HNO_3+	NH_3	0.455	2655	21	1.12	239
7.	15% NO_2	N_2H_4	0.769	3022	20	1.26	257
8.	HNO_3+	NH_3	0.465	2600	21	1.12	237
9.	22% NO_2	$N_2H_2(CH_3)_2$	0.385	3144	22	1.23	250
10.	N_2O_4	N_2H_4	0.909	3005	19	1.20	263
11.		NH_3	0.476	2978	21	1.03	252
12.		C_2H_5OH	0.769	3116	23	0.99	248
13.		NH_3	0.769	2988	19	0.88	266
14.	O_2	$N_2H_2(CH_3)_2$	0.769	3289	19	0.96	276
15.		N_2H_4	1.429	3072	18	1.06	282
16.		H_2	0.286	2755	9	0.26	364
17.	O_3	H_2	0.312	2944	8.3	0.26	393

The charge densities of atoms were calculated to within ±0.02 of the electron charge. The bond length between the atoms and angles were calculated with an accuracy of ±0.01 nm and ±10°, respectively.

The initial models of the reactive fuels were specified by the following set parameters: number of atoms (from 2 to 17), number of orbitals (from 2 to 80), total charge of the models $\sum q_m = 0$, and multiplicity $M = 2S + 1$ (S is the overall spin equal to zero for all the models, hence M equals unity).

The total energy was minimized by gradient technique with the fragment optimization described in [2].

The calculations are performed assuming that the molecule is isolated in a gas phase. Such approximation is possible, since calculated quantum-chemical parameters of acidity (q_{H^+}, pK_α) are compared with the data (Tab. II) for some fuel mixtures received in supposition, that the process of combustion is adiabatic, gases are ideal, their expansion is non-entropic, their nozzle is ideal, and speed of dissociation is constant during its expansion [1].

RESULTS AND DISCUSSION

Though CNDO/2 calculations of some models of reactive fuels (H_2, N_2H_4, NH_3, H_2O_2, B_2H_6, *etc.* [3]) were performed, there were not systematized studies in this area. That is why it is necessary to analyze the results received and their systematization to study behaviour of reactive fuels in oxidation-reconstruction reactions further more detailed.

The quantum-chemical characteristics of models of reactive fuels are represented in Table II, and electronic structures and optimized geometries at all parameters are illustrated in Figure 1.

For hydrogen (H_2, Fig. 1a) the inter-nuclear distance is 0.076 nm (literary data 0.07414), the energy of bond is 312 kJ/mole, where as the energy of dissociation is 436 kJ/mole. The maximum charge on hydro-

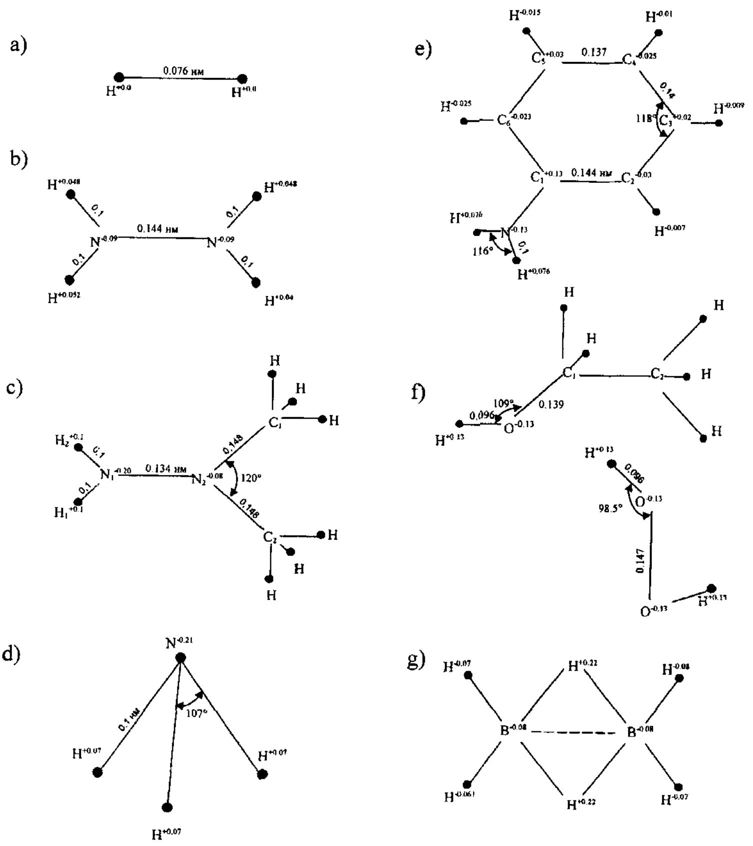

FIGURE 1 Electronic structure and optimized geometry of models of reactive fuels: hydrogen (a), hydrazine (b), dimethyl-hydrazine (c), ammonia (d), aniline (e), ethanol (f), hydrogen peroxide (g) and diboron (h).

gen atom q_{H^+} is equal to 0, which corresponds to pKa = 45 (Tab. I). The boiling point is −183°C. Out of all considered fuels H_2 possesses the minimum acidic strength, but herewith out of all oxidizers its specific impulse J_{sp} is maximum. One of the properties of the liquid hydrogen is that it has the minimum temperature of combustion and the minimum molecular weight of the products of combustion. But in consequence of very small specific weight of hydrogen, as well as needed to careful thermoinsulating the tanks the constructive attitude in hydrogen rockets is below than in rockets using organic combustible once. Hydrogen is dangerous in use and less suitable in keeping.

Hydrazine (N_2H_4, diamid, Fig. 1b). The maximum charge of the hydrogen atom of diamid $q_{H^+} = +0.05$ and the value of universal acidity index $pK_\alpha = 37$ testify to N_2H_4 possessing rather low acidic strength, as a reactive fuel characterized by analogy H_2 by rather high values of specific impulses J_{sp}. Hydrazine is a rather wide spread type of fuel and it is usually used with nitric acid. The shortcoming of N_2H_4 is poisonous smoke, forming during burning.

Asymmetric dimethyl-hydrazine ($N_2H_4(CH_3)_2$, Fig. 1c). The model is derived from the hydrazine. Parameters of acidity are $q_{H^+} = +0.10$ and $pK_\alpha = 27$. The specific impulse value of dimethyl-hydrazine is less differed from specific impulse hydrazine.

Ammonia (NH_3, Fig. 1d). The molecule has a form of a proper pyramid. The bonds N—H are polar. The charges q_{H^+} owing to good symmetry are identical on hydrogen atoms and are equal to +0.07 on each one. The existence of the molecule NH_3 is warranted by rather considerable quantities $E_0 = -35998$ kJ/mole and $E_{bon} = -2237$ kJ/mole. Ammonia is rather weak-acidic reactive fuel juidging by the charges on hydrogen atoms and by meaning of $pK_\alpha = 33$.

Aniline ($C_6H_5NH_2$, Fig. 1e). Maximum positive charge on hydrogen atom in aniline is concentrated on H-atoms of NH_2-group – $q_{H^+} = +0.08$. The molecule is stable since it has the following meaning of the energy $E_0 = -153522$ kJ/mole and $E_{bond} = -18179$ kJ/mole. The meaning $pK_\alpha = +31$ show that $C_6H_5NH_2$ is a rather weak H-acid.

Ethyl alcohol (C_2H_5OH, Fig. 1f). It possesses minimum specific impulse, the low value of acidity $pK_\alpha = 16$ and rather high value of charge $q_{H^+} = 0.13$ out of all considered fuels. It is interesting that addition of 25% water relatively little decreases specific impulse. The optimum mixture of ethyl alcohol, water and oxygen can have specific impulse, which is near toward theoretical value, when fuel does not consist of water. Such fuel mixture is relatively safe in turning, suitable for keeping, has rather low specific weight and is not much expensive.

Hydrogen peroxide (H_2O_2, Fig. 1g). It is weak acid $pK_\alpha = +11.6$ (in H_2O, 20°C), $pK_\alpha = +16$ (calculation CNDO/2 in gas phase, 273°C). As one-component fuel H_2O_2 in the line of reactive fuels is characterized by rather low meaning of specific impulse – J_{sp}, and quite independent on the nature of oxidizer (Tab. II).

Diboron (B_2H_6, Fig. 1h). This model is characterized by the following meanings $E_0 = -33198$ kJ/mole, $E_{bond} = -7365$ kJ/mole which testifies to rather high stability of diboron. Maximum charge on atom of hydrogen is $q_{H^+} = +0.22$ and according to correlative dependence $pK_\alpha(q_{H^+})$ [4] $pKa(B_2H_6) = +4.4$. Enthalpy of B_2H_6 consumption considerably exceeds enthalpy of combustion, that is why diboron (B_5H_9 – pentaboron and $B_{10}H_{14}$ – decaboron as well), are of great interest as long-range highly effective rocket fuel. Their wide usage however is restrained by complexity of production and extreme toxicity.

The performed quantum-chemical calculation of models of rocket fuels by classical semi-empirical CNDO/2 method in Santry-Poplar-Seagal parametrization with optimization in all parameters by gradient method in approaching of an isolated molecule in gas phase allowed to find optimum geometry and electronic structures (Fig. 1) and appreciate their acidic strength. The analysis of quantum-chemical parameters of acidity (q_{H^+}, pK_α) of models testifies to the that all fuels are rather weak acidic H-acids. Maximum charges of the hydrogen atoms of fuels changes in rather wide range $0 \leq q_{H^+} \leq +0.22$, and according to [4] the range of meanings of universal indexes of acidity is $+4.4 \leq pK_\alpha \leq 45$. Liquid H-hydrogen is characterized by minimum meaning $q_{H^+} = 0$, diboron – by maximum one – $q_{H^+} = +0.22$. By analogy, reactive fuel diboron possesses the greatest acidity – $pK_\alpha = +4.4$, liquid hydrogen possesses the lowest acidity – $pK_\alpha = 45$. It should be marked that the following dependence is observed in the line of rocket fuels under investigation: $H_2, N_2H_4, NH_3, C_2H_5NH_2, N_2H_2(CH_3)_2, OHC_2H_5$, H_2O_2, B_2H_6. At decreasing of maximum charge q_{H^+} on hydrogen atom of reactive fuels corresponds the increasing of their acidic strength (Tab. I). Besides that, the performed calculation of models and comparison of the received results with the data in Table II proves possible existence of correlative dependencies of acidic strength of fuels on their physical and chemical parameters. Which are: specific impulse $J_{sp} = c/g$ (where c is speed of gases outflow, in m/s; g – the acceleration of free fall, in m/s^2); δ – specific weight of fuel mixtures; T – the temperature of combustion, °K; $\varphi = W_{comb}/W_{oxid}$ – ratio of fuel weight to the weight of oxidizer. With great trust-worthiness one can observe correlative dependence pK$_\alpha$ (and this corresponds to the decrease of maximum charge on hydrogen atom – q_{H^+} and acidic strength of rocket fuels), specific impulse – J_{sp} increase (Fig. 2). And by this φ and T varied in rather wide ranges: $0.286 \leq \varphi \leq 1.429$, $2755°K \leq T \leq 3522°K$. Liquid hydrogen at $q_{H^+} = 0$ possesses the maximum specific impulse. By that the temperature of combustion H_2 is T, δ – specific weight of fuel, φ-ratio of fuel weight to the weight of oxidizer and M_{burn} – molecular weight of combustion products (that is very important from ecological point of view) are minimum. And it doesn't depend on the nature of oxidizer. Besides H_2 by known enumerated parameters – T, δ, φ, M_{burn}, J_{sp} and calculated by quantum-chemical pK$_\alpha$, q_{H^+} is twice or sometimes thrice as large as the nearest fuel, for example, NH_3. That is to say, from the point of view of quantum chemistry H_2 is one of the best liquid reactive fuels.

The following correlations are established to oxygen (Fig. 2):

$$J_{sp} = J_{sp,0}[0.99 - 4.78(q_{H^+}) + 19.52(q_{H^+})^2]; \quad R = 0.971;$$

$$J_{sp} = J_{sp,0}[0,9 - 0,02(\mathrm{pK}_\alpha) + 0,0005(\mathrm{pK}_\alpha)^2]; \quad R = 0.957;$$

Here: R is the coefficient of correlation; $J_{sp,0} = 364$ (s) – the maximum specific impulse.

Other parameters (D – the dipole moments; E_0 – the total energy; E_{bond} – the energy of bonds; δ – specific weight of fuel mixtures; T – temperature of combustion; φ – ratio of fuel weight to the weight of oxidizer; M_{burn} – average molecular weight of burning products;) do not give satisfactory correlations. Even received correlations are not uniquely defined of the given dependence. For example: correlation $J_{sp}(q_{H^+})$ gives an increase of specific impulse from negative charge of hydrogen atom in molecule, but it is known that liquid hydrogen possesses maximum impulse from $q_{H^+} = 0$. That is why these correlations can be used only at interval of charges on hydrogen atom from

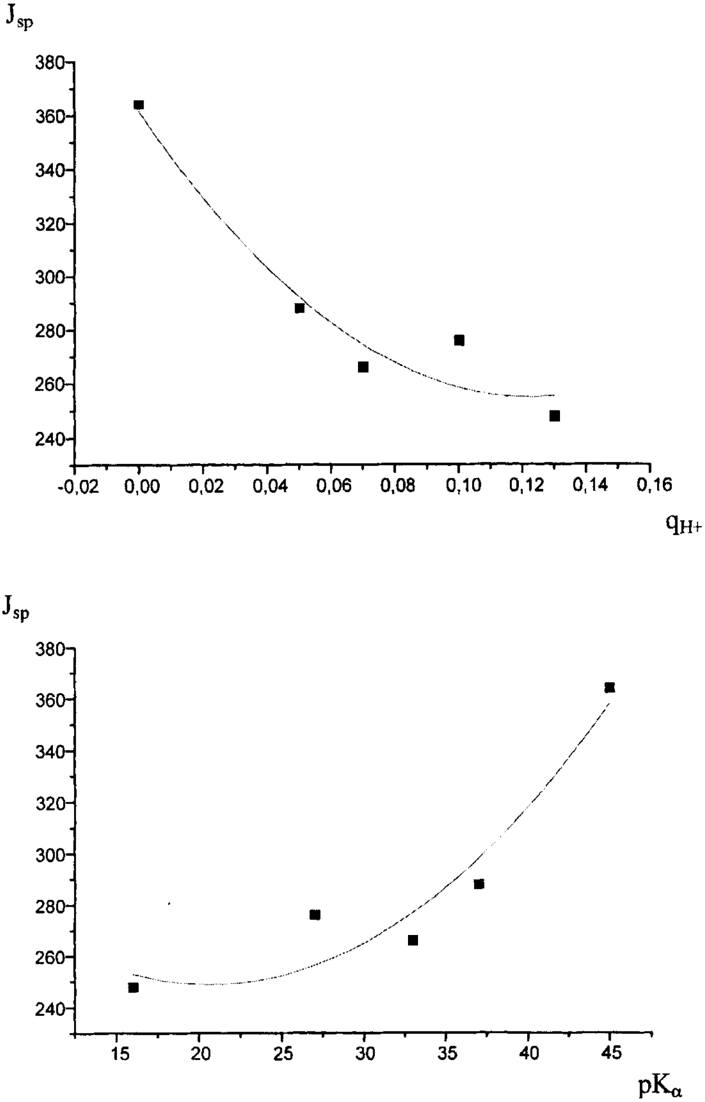

FIGURE 2 Correlative dependences of maximum hydrogen charge q_{H^+} and universal index of acidity pKa on specific impulse J_{sp}.

+0.0 to +0.18. And the expedient interest is to define more general functional dependence of combustion parameters from parameters characterizing construction of materials and parameters of acidity.

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