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CALCULATION OF THE THERMODYNAMIC PARAMETERS OF THE REACTION BETWEEN ACRYLOYL CHLORIDE AND WATER BY DENSITY FUNCTIONAL THEORY

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Purpose. Study of thermodynamic properties of acryloyl chloride to predict the danger if the acryloyl chloride is extinguished by water.

Methods. Thermodynamic properties (including enthalpy, free energy, entropy and heat capacity at constant pressure) of acryloyl chloride at vapor phase at 1.0 atm pressure and temperature range from 298.15 to 1000.00 K in steps of 100.00 K are determined by DFT calculations using PBEPBE functional. As the basis set 6-311G++(d,p) is used.

Findings. Free energy, and heat of reaction between acryloyl chloride and water in the fire (at the same temperature range and pressure) have been calculated. In temperature range from 298.15 to 1000.00 K, the reaction between acryloyl chloride and water is exothermic. So, if firefighters use water to fight the fire of acryloyl chloride, a large amount of heat will be released. This heat makes the fire is more dangerous and difficult to fight.

Application field of research. The results of research can be used in prediction the hazard of burning of acryloyl chloride and ways of extinguishing it.

Keywords: burning of acryloyl chloride, reaction with water, thermodynamic properties, DFT, acryloyl chloride, extinguishing by water.

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1. Introduction

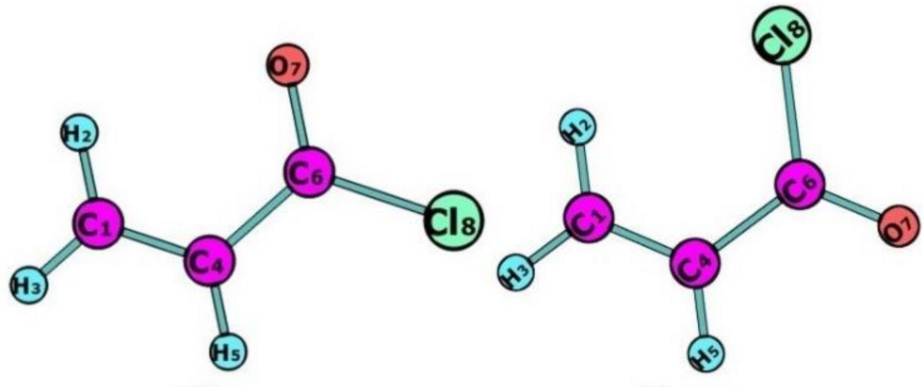
The history of density functional theory (DFT) began in 1926 with the creation of Thomas and Fermi theory. At first, this theory was very primitive, the application of this method often gave bad results [1]. Then, with the contributions of Slater, Hohenberg and Kohn with the Kohn - Sham equation, DFT has experienced a flourishing development stage and gained some certain achievement. Over the past thirty years, DFT has become a much used widely tool in computation quantum sciences such as physic and chemistry [1; 2] in which DFT is a computational quantum mechanical modelling method used to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. The properties of a many-electron system can be determined by using DFT with functionals, i.e., functions of another function [2]. In computation chemistry, the electronic structure of a system is computed by DFT with an exchange correlation functional and a basis set. The choice of the exchange correlation functional and the basis set depends on the system to be calculated. From the electron structure, some properties of the system are determined such as: electronegativity and the electronic chemical potential, global hardness and softness, thermodynamic properties. etc. Based on these properties, the chemical properties of the system can be accurately predicted [2; 3]. Therefore, studies based on DFT can be applied in many other sciences closely related to chemistry, such as material science and fire science.

The development of fire science had been started since ancient times. Until the mid-20th century, the fire science had really evolved along with the development of other sciences, especially the basic sciences such as Mathematics, Physics, and Chemistry [4]. Fire science is an integrated field of many sciences of which chemistry is the core. Based on chemistry, specifically the patterns of the combustion reaction, the properties of the combustible are determined to give effective methods of extinguishing fires. One of the most widely recognized effective fire-fighting methods since ancient times is the use of water. Water is one of common fire extinguishing agents because it is very popular, safe, and cheap. The fire extinguishing mechanism of water is mainly to take away the heat released from combustion of fuel [5]. In the heat absorption process, water vaporizes to steam which reduces concentrations of oxygen and fuel at vapor phase. With these advantages, water is called “gold key” for extinguishing all type of fire. However, some materials and some chemical compounds react actively with water such as calcium carbide, alkaline metal, some organic compound. These reactions are usually exothermic reactions and produce flammable products. So, water is not a suitable extinguishing agent for all types of fires, especially chemical fires when agents can react with water, such as acryloyl chloride.

Acryloyl chloride, has also known as 2-propenoyl chloride or prop-2-enoyl chloride or acrylic acid chloride, is the organic compound with the formula CH_2=CHCO(Cl) and CAS number 814 – 68 – 6. With 298.15 K temperature and 1.0 atm pressure of air, it is a colorless or pale-yellow liquid [6–8]. Acryloyl chloride is the toxic compound, highly flammable and can react with water to give hydrogen chloride and acrylic acid [6–9]. Acryloyl chloride is mainly used as a monomer and an intermediate in the synthesis of acrylate compounds. It is used in the manufacture of plastics, absorbents, anti-fog agents, coating materials, extended drug release capsules and paints [9; 10]. On other hand, the boiling point of acryloyl chloride is 167 °F at 760 mm Hg pressure of air (about 75 °C at 1.0 atm pressure of air) [6]. So, in the fire where is normally over 500 °C temperature [11], acryloyl chloride exists in the vapor state. With the above characteristics, acryloyl chloride is a common chemical widely used in the organic synthesis industry and the leakage of this compound will face many dangers to humans and the environment, especially when leakage occurs in a fire. In a fire, acryloyl chloride reacts with oxygen and releases very much heat which can cause rollover or flashover [7; 12]. To prevent these negative phenomena, the implementation of fire-fighting measures is imperative. However, acryloyl can react with water, so using water to extinguish the fire of this compound can aggravate the fire, so this work should be considered carefully from a scientific perspective. One of the methods to assess the danger of reaction between acryloyl chloride and water is using its thermodynamic properties in the temperature range of a fire. Thermodynamic characteristics of reaction between acryloyl chloride with water are determined by thermodynamic properties of reactants and product including acryloyl chloride, water, hydrogen chloride and acrylic acid. The thermodynamic properties of acryloyl chloride have been determined at 298.15 K temperature or lower temperatures in some previous studies [13], and some thermodynamic properties at other higher temperatures have been determined by semi – experimentation [14]. However, this data is not enough to determine the thermodynamic properties of reaction between acryloyl chloride with water in a fire. Therefore, determining the thermodynamic properties of acryloyl chloride and its reaction with water at higher temperatures is very important to predict the possibility of using water to extinguish a fire of acryloyl chloride and this work has become easier by using quantum chemistry with DFT calculations. This article focuses on clarifying this issue by using DFT calculations.

2. Calculation method

There are two planar geometric isomers of acryloyl chloride including *cis* - acryloyl chloride and *trans* - acryloyl chloride (Fig. 1) and other nonplanar isomers [14; 15]. In some early studies with gas-phase electron diffraction (GED), microwave (MW), and some spectra such as IR and Raman, planar trans structure of acryloyl chloride was confirmed which is more stable than cis structure and other nonplanar structures [14,15]. So, in this study, planar *trans* – acryloyl chloride structure is used to calculate thermodynamic properties. Since the mechanism of reaction between acryloyl chloride with water chloride is the substitution of the chlorine atom by the OH group, structure of acrylic acid is used to calculate which is *trans* structure (Figure 2). Since the temperature of the fire is normally over 500 °C, acryloyl chloride (boiling point is 75 °C [8]), water (boiling point is 100 °C), hydrogen chloride (boiling point is -85.05 °C) and acrylic acid (boiling point is 141 °C [8]) exist in vapor phase at 1.0 atm pressure of air, so their thermodynamic properties are calculated at vapor phase and 1.0 atm pressure.



Cis Trans

Figure 1. – Two geometric isomers of acryloyl chloride

The initial structures of each compound are designed by using GaussView 03 program package and all calculations in this study are performed by using Gaussian 03 program package [16]. Optimization process and frequency calculation has been carried out for each of reactant molecules (including acryloyl chloride and water) and product molecules (including hydrogen chloride and acrylic acid) of reaction between acryloyl chloride and water. Determining a reasonable calculation method is a mandatory requirement in any study. In this study, the method DFT is used. Although DFT method is a reliable method commonly used to calculate and determine the molecular structure and other properties of acryloyl chloride and other acrylate in some recent studies, [13,14,17] the re-validation of this method is extremely important to have a more objective view of the suitability of the calculation method. In this study, the total energy of acryloyl chloride molecular is calculated by DFT and other methods such as Hartree-Fork (HF), The second order of Møller-Plesset (MP2) with using the same basis set. The basis set is used which is 6-311G++(d,p). The total energy results are compared to confirm the reliability of the DFT method. Because of the similarity of structures between acryloyl chloride and acrylic acid, in the chosen method a determined structure is used and thermodynamic properties of acryloyl chloride are calculated which is used for acrylic acid calculating. On the other hand, structure of water and hydrogen chloride are calculated by DFT method which are good results [18–22].

Then, all structures of *trans* – acryloyl chloride, water, hydrogen chloride and acrylic acid were optimized, which are used to calculate and determine frequency values of vibrations. Based on these, frequency values of vibrations of each molecule was calculated, thermodynamic properties at 1.0 atm pressure and temperature range from 298.15 to 1000.00 K in steps of 100.00 K are determined. All thermodynamic properties of each compound are used to calculate thermodynamic peculiarities of this reaction by using the following equations [19]:

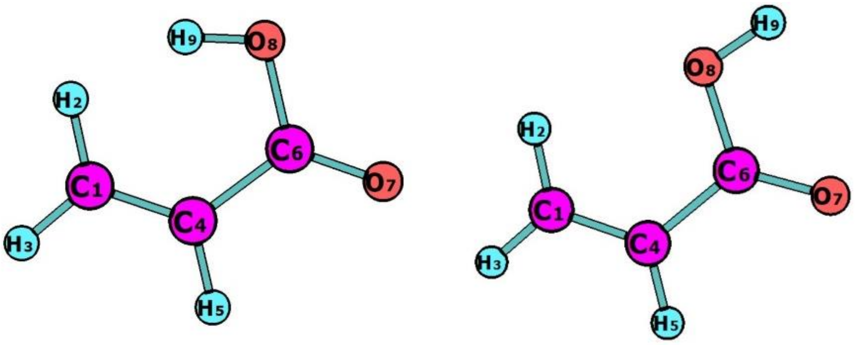
$$\Delta G_{Reaction,\mathrm{T}} = \sum_{i\geq 1}(E_{tot}+G_{\mathrm{cor,T}})_i^{Product} - \sum_{j\geq 1}(E_{tot}+G_{\mathrm{cor,T}})_j^{Reactant} \qquad (1)$$

$$\Delta S_{Reaction,\mathrm{T}} = \sum_{i\geq 1} S_{i,T}^{Product} - \sum_{j\geq 1} S_{j,T}^{Reactant} \qquad (2)$$

$$\Delta H_{Reaction,\mathrm{T}} = \sum_{i\geq 1}(E_{tot}+H_{\mathrm{cor,T}})_i^{Product} - \sum_{j\geq 1}(E_{tot}+H_{\mathrm{cor,T}})_j^{Reactant} \qquad (3)$$

with E_{tot} is total electronic energy at 0 K of each molecule, $\Delta G_{Reaction,\mathrm{T}}$, $\Delta S_{Reaction,\mathrm{T}}$ and $\Delta H_{Reaction,\mathrm{T}}$ are variations of free energy, entropy and enthalpy of reaction, enthalpy of reaction at temperature T; $G_{\mathrm{cor,T}}$ and $H_{\mathrm{cor,T}}$ are free energy correction and enthalpy correction at temperature T, in which $G_{\mathrm{cor,T}}$ and $H_{\mathrm{cor,T}}$ including zero point vibration energy (ZPVE).

Enthalpy of reaction has also called as heat of reaction. Values of heat of reaction are used to assess the heat property of a chemical reaction. Endothermic reaction is reaction in which heat is absorbed and exothermic reaction is reaction in which heat is produced. Free energy of reaction is used to assess the possibility of a chemical reaction according to thermodynamic conditions.



(a) The first planar structure (b) The second planar structure

Figure 2. – Two planar structure of *trans* – acrylic acid

3. Results and discussion

3.1. Validation of DFT method

Total energy values which are determined from DFT method with different functionals (such as B3LYP, B3PW91, HCTH, PBEPBE, PBE1PBE, LSDA) have been compared with the total energies which are determined by other method. They are shown in Table 1. The results are calculated by using DFT method that shows the more accuracy (exception DFT method with using LSDA functional). The result is determined by DFT method with HCTH functional (DFT/HCTH method) which is the most accuracy with E_{tot} is -651.6318658 Hartree, that is the lowest energy. As we know that, with the same basis set, better calculation method is the method which gives geometric structure containing minimum energy [14; 21], DFT/HCTH method is likely to produce more accurate geometry structure.

Table 1. – Comparison of total energy of optimized structure of acryloyl chloride with other study

Method	Total energy of *trans* - acryloyl chloride *(Hartree)*	Relative error (%) from DFT/HCTH method (%)
DFT/HCTH/6-311G++(d,p)	-651.6318658	
DFT/B3LYP/6-311G++(d,p)	-651.6129335	0.003
DFT/LSDA/6-311G++(d,p)	-649.4281394	0.338
DFT/PBEPBE/6-311G++(d,p)	-651.1840191	0.069
DFT/PBE1PBE/6-311G++(d,p)	-651.2197143	0.063
DFT/B3PW91/6-311G++(d,p)	-651.4781636	0.024
HF/6-311G++(d,p)	-649.7521641	0.288
MP2/6-311G++(d,p)	-649.7490645	0.289

Comparing with DFT/HCTH method, 0.338 % is the highest relative error which has been calculated by the DFT/LSDA method and the lowest relative error is 0.003 %, it has been calculated by DFT/B3LYP method. MP2 and HF method are non DFT method, they show results with relative errors which are larger relative errors of other DFT method. However, these relative errors are the small values, so several other parameters need to be calculated to determine the suitable method. Suitable method is method that shows the most approximate results comparing with semi - experimental results. Specifically, in this study, thermodynamic parameters including entropy and heat capacity at constant pressure in 298.15 K temperature which are calculated. These results are shown at Table 2 and they are compared with semi - experimental result. Entropy and heat capacity at constant pressure in 298.15 K temperature of acryloyl chloride was determined by Compton et al. by using semi-experimental method in 1981 [14].

Table 2. – Comparison of entropy and heat capacity at constant pressure in 298.15 K temperature of acryloyl chloride with empirical results

Method	S ($J \cdot mol^{-1} \cdot K^{-1}$)	C_P ($J \cdot mol^{-1} \cdot K^{-1}$)	Relative error (%) from semi-experimental result of entropy	Relative error (%) from semi-experimental result of heat capacity at constant pressure
DFT/HCTH/6-311G++(d,p)	311.69	80.87	1.707	2.805
DFT/B3LYP/6-311G++(d,p)	310.29	80.02	2.148	3.822
DFT/LSDA/6-311G++(d,p)	310.00	80.94	2.239	2.716
DFT/PBEPBE	311.85	81.62	1.656	1.899
DFT/PBE1PBE	309.26	79.29	2.472	4.700
DFT/B3PW91/6-311G++(d,p)	309.87	79.72	2.280	4.183
HF/6-311G++(d,p)	306.12	75.43	3.463	9.339
MP2/6-311G++(d,p)	313.23	80.46	1.220	3.293
Semi - experimental method [14]	317.10	83.20	N/A	N/A

The relative errors from semi - experimental result of calculated entropy values which increase in the direction: MP2 < DFT/PBEPBE < DFT/HCTH < DFT/B3LYP < DFT/LSDA < DFT/B3PW91 < DFT/PBE1PBE < HF, on the other hand, the relative error from semi - experimental result of calculated heat capacity at constant pressure values which increase in the direction: DFT/PBEPBE < DFT/LSDA < DFT/HCTH < MP2 < DFT/B3LYP < DFT/B3PW91 < DFT/PBE1PBE < HF. MP2 method is the best method to calculate entropy with the relative error from semi - experimental result is 1.22 % but it is not the best method for calculating heat capacity at constant pressure with the relative error from semi - experimental result is 3.293 %. This relative error is more than relative error of entropy of DFT/PBEPBE, DFT/LSDA and DFT/HCTH method with relative errors are 1.899, 2.716 and 2.805 % respectively. The best method to calculate heat capacity at constant pressure that is DFT/PBEPBE with the relative error from semi - experimental result is 1.899 %. Although DFT/HCTH shows the most minimum total electronic energy, it is not the best method for calculating thermodynamic properties of acryloyl chloride. From the results above, DFT/PBEPBE method is the best DFT method for calculating for calculating thermodynamic properties acryloyl chloride. So, in this study, thermodynamic properties acryloyl chloride in temperature range from 298.15 to 1000.00 K in steps of 25.00 K at 1.0 atm pressure are calculated by DFT/PBEPBE method.

3.2. Optimized geometry parameters of acryloyl chloride

Values of bond lengths and bond angles of *trans* – acryloyl chloride planar structure was calculated by DFT/PBEPBE method with 6-311G(d,p) basis set level which are shown in Table 3 and Figure 3.

Table 3. – Bond length and bond angle parameters of trans – acryloyl chloride planar structure

Bond	Values (Angstrom, Å)	Angle	Values (degrees)
$C_1 – C_4$	1.341	$O_7C_6Cl_8$	119.40
$C_4 – C_6$	1.475	$C_4C_6Cl_8$	115.21
$C_6 – O_7$	1.198	$C_4C_6O_7$	125.40
$C_6 – Cl_8$	1.834	$C_4C_1H_2$	121.72
$C1 – H_3$	1.092	$H_2C_1H_3$	117.81
$C1 – H_2$	1.091	$H_3C_1C_4$	120.47
$C_4 – H_5$	1.094	$C_1C_4C_6$	126.21
		$C_6C_4H_5$	112.29
		$C_1C_4H_5$	121.49

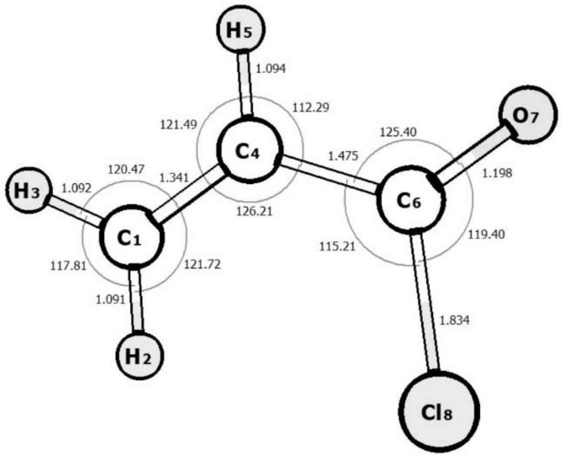


Figure 3. – *Trans* – acryloyl chloride planar structures are determined by DFT/PBEPBE using 6-311G++(d,p) basis set

The distance between centers of the two covalently bonded atoms is the bond length. The value of the bond length between two atoms is usually less than the sum of the radius of the two atoms. The values of carbon and hydrogen bond lengths in acryloyl chloride are 1.092 Å ($C_1 – H_3$), 1.091 Å ($C_1 – H_2$) and 1.094 Å ($C_4 – H_5$). These values are almost identical. Bond length of C4 – H5 is larger than bond lengths of $C_1 – H_2$ and $C_1 – H_3$, that is likely to be caused by the influence of the remaining substituent of C4 atom. This substituent is C(=O)Cl group of atoms. Bond length value of $C_4 – C_6$ is 1.475 Å which is larger than bond length value of $C_1 – C_4$ (1,341 Å). The type of bond (single and double bond) is the main reason of having a difference in this bond length value. $C_1 – C_4$ bond is the double bond and $C_4 – C_6$ bond is the single bond. This difference is caused by generally bond length decreases in the order: single bond > double bond > triple bond [15]. In this C(=O)Cl group of atoms, $C_6 – O_7$ bond length value is 1.198 Å which is smaller than 1.834 Å value of $C_6 – Cl_8$ bond length, that is caused by the difference of their bond order (double bond of $C_6 – O_7$ and single bond of $C_6 – Cl_8$) and the difference between radius of oxygen atom and radius of chlorine atom.

Other important parameter for the optimized structure is bond angle because it has the effect on the molecule and even rise the bond angle in result of reducing micro tensile bond strength [21; 23]. It is the main factor to define the shape of the molecule. Sum of values of three bond angles around C1 atom is 360 degrees, which confirms that the atoms including C_1, C_4, H_2, H_3 atom are coplanar. In which, the value of C_4C1H_2, H_2C1H_3, and H_3C1C_4 bond angle is 121.72, 117.81 and 120.47 degree respectively. The difference of bond angles around C1 atom is caused by the radius of the hydrogen atom, which is smaller than the radius of the carbon atom. Sum of values of three bond angle around C_4 atom and sum of values of three bond angles around C6 atom are also similar sum of values of three bond angle around C_6 atom. They also have sum of bond angle values which is 360 degrees. It confirms that all the atoms in the acryloyl chloride molecule are coplanar. This result is completely consistent with the results of previous structural studies of acryloyl chloride by other methods [13; 15].

3.3. Calculation results of thermodynamic properties of acryloyl chloride

Entropy (S), heat capacity at constant pressure (C_P), sum of electronic and thermal enthalpies ($E_{tot} + H_{cor}$, including zero point energy), sum of electronic and thermal free energies ($E_{tot} + G_{cor}$, including zero point energy) of trans-acryloyl chloride in temperature range from 298.15 to 1000.00 K in steps of 100.00 K are determined by DFT/PBEPBE, which are shown in Table 4. These results are compared with semi-experimental result which was determined by Compton et al. [14].

Table 4. – S, C_P, ($E_{tot} + H_{cor}$), ($E_{tot} + G_{cor}$) of trans - acryloyl chloride with temperature range from 298.15 to 1000.00 K in steps of 100.00K are determined by DFT/PBEPBE and compared with semi-experimental result

T (K)	DFT/PBEPBE/6-311G++(d,p)				Semi-experimental result [14]		Relative error (%) from semi-experimental result	
	S ($J·mol^{-1}·K^{-1}$)	C_P ($J·mol^{-1}·K^{-1}$)	$E_{tot} + H_{cor}$ (Hartree)	$E_{tot} + G_{cor}$ (Hartree)	S ($J·mol^{-1}·K^{-1}$)	C_P ($J·mol^{-1}·K^{-1}$)	S (%)	C_P (%)
298.15	311.85	81.62	-651.126649	-651.162047	317.1	83.2	1.656	1.899
300.00	312.36	81.94	-651.126591	-651.162267	317.6	83.5	1.650	1.868
400.00	338.12	97.43	-651.123168	-651.174659	343.7	98.1	1.624	0.683
500.00	361.27	110.05	-651.119210	-651.187980	367.0	110.4	1.561	0.317
600.00	382.26	120.19	-651.114820	-651.202140	388.0	120.4	1.479	0.174
700.00	401.43	128.43	-651.110082	-651.217063	407.2	128.6	1.417	0.132
800.00	419.04	135.26	-651.105058	-651.232686	424.8	135.5	1.356	0.177
900.00	435.31	141.00	-651.099796	-651.248953	441.1	141.3	1.313	0.212
1000.0	450.43	145.87	-651.094333	-651.265817	456.3	146.2	1.286	0.226

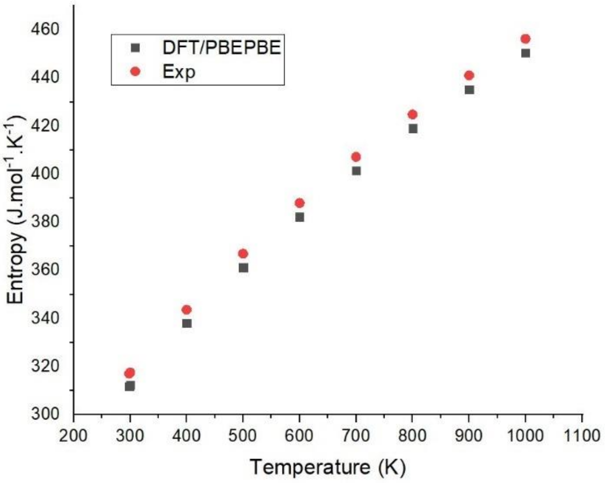


Figure 4. – The dependence of calculated reaction entropy on the temperature in comparison with experiment

There are relatively small differences between entropy values which are calculated by using DFT/ PBEPBE with the semi-experimental entropy values. The highest relative error of entropy is 1.656 % at 298.15 K temperature and the lowest relative error is 1.28 6%. These relative errors tend to decrease with increasing temperature. From the results of entropy shown at Table 4 and Figure 4 the entropy of Acryloyl chloride increases with increasing temperature. Therefore, increasing temperature increases the diffusion of Acryloyl chloride, because the diffusion of a gas increases with increasing entropy [24–26]. So, in a fire, with a rapid increase in temperature, acryloyl chloride will diffuse more strongly, which can cause dangerous phenomena such as flashover or explosion [12]. However, in the temperature range from 298.15 to 1000 K, the entropy values increase slowly, about 50 %. This slow increasing is explained by structure of acryloyl chloride, in which there are only 7 valent bonds. So, the diffusion of acryloyl chloride increases slowly. For this reason, the probability of rollover and flashover are very low without convection [12].

With heat capacity at constant pressure values, their relative errors are compared with semi - experimental results which are relatively small (about under 2 %). The highest relative error of heat capacity at constant pressure is 1.899 % at 298.15 K temperature. Same as entropy, these relative errors tend to decrease with increasing temperature. From the results of heat capacity at constant pressure shown at Table 4 and Figure 5, the entropy of acryloyl chloride increases with increasing temperature.

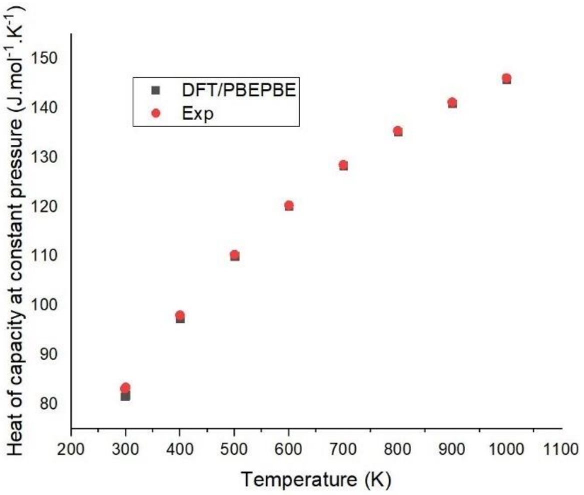


Figure 5. – The dependence of calculated heat capacity at constant pressure on the temperature in comparison with experiment

3.4. Result of optimized geometries of acrylic acid, water and hydrogen chloride

Since acrylic acid structure is similar to structure of acryloyl chloride, the method is used to determine optimized geometry of molecule and calculate thermodynamic properties which is DFT/PBEPBE. Same as acryloyl chloride structure, acrylic acid structure is *trans* structure and this structure is relatively planar. The flatness of the *trans* acrylic acid structure depends on the rotation of the $O_8 – H_9$ bond around the $C_6 – O_8$ bond axis. This rotation is represented by the value of the $O_7C_6O_8H_9$ dihedral angle (Fig. 6). In this study, energy of *trans* acrylic acid structures with other values of the $O_7C_6O_8H_9$ dihedral angle are calculated by DFT/PBEPBE/6-311G++(d,p) method to determine the best structure of *trans* acrylic acid. The best structure is the structure which contains minimum energy [21]. The results of total electronic energy with other values of the $O_7C_6O_8H_9$ dihedral angle are shown in Table 5. Value of the $O_7C_6O_8H_9$ dihedral angle is in value range from -180 to 180 degree in 30 degrees steps.

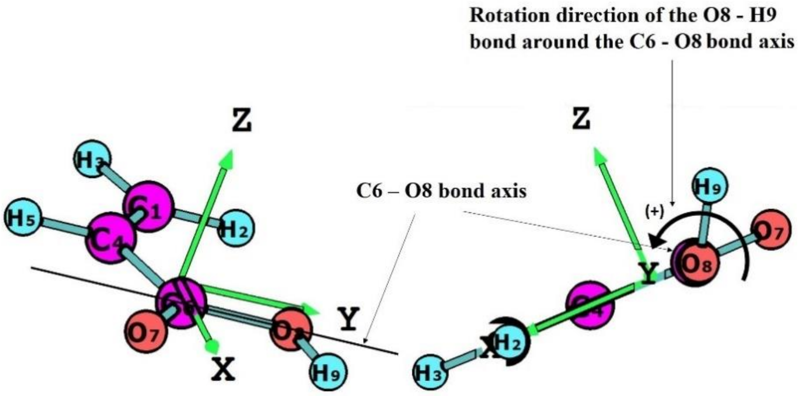


Figure 6. The scheme of rotation of the $O_8 – H_9$ bond around the $C_6 – O_8$ bond axis

From calculation results of total electronic energy shown in Table 5 and Figure 7, there are obtained two planar structures of *trans* acrylic acid including the first planar structure and the second planar structure which are shown in Figure 2. In which, -266.9444380 Hartree is value of total electronic energy of the second planar structure which is smaller than of total electronic energy of the first planar structure (-266.9311143 Hartree). Moreover, this second planar structure also has a smaller energy than energy of other nonplanar structures. So that, it is chosen structure to optimize geometry structure of acrylic acid.

Table 5. – Total electronic energy of trans acrylic acid structures with other values of the $O_7C_6O_8H_9$ dihedral angle

Value of the $O_7C_6O_8H_9$ dihedral angle (Degree)	Total electronic energy (Hartree)	Structure
180	-266.9311143	The first planar structure
150	-266.9297593	Nonplanar structure
120	-266.9249334	Nonplanar structure
90	-266.9230360	Nonplanar structure
60	-266.9299278	Nonplanar structure
30	-266.9398731	Nonplanar structure
0	-266.9444380	The second planar structure
-30	-266.9398338	Nonplanar structure
-60	-266.9299033	Nonplanar structure
-90	-266.9230280	Nonplanar structure
-120	-266.9249410	Nonplanar structure
-150	-266.9297690	Nonplanar structure
-180	-266.9311143	The first planar structure

Note. The negative sign of the dihedral angle value is the rotation of the $O_8 – H_9$ bond around the $C_6 – O_8$ bond axis in the opposite direction to the conventional direction which is shown in Figure 6.

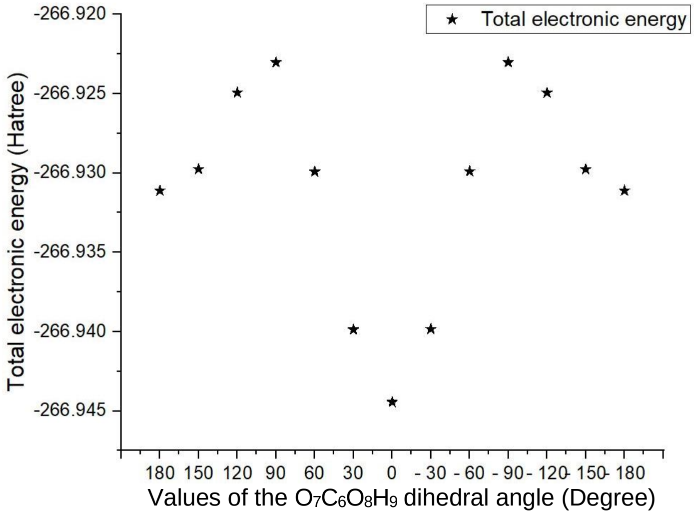


Figure 7. – Diagram of total electronic energy of *trans* acrylic acid structures with other values of the $O_7C_6O_8H_9$ dihedral angle

Optimized geometry structure of *trans* acrylic acid is determined by DFT/PBEPBE/ 6-311G++(d,p). Values of bond lengths and bond angles of *trans* acrylic acid are shown at Table 6 and Figure 8.

Table 6. – Bond length and bond angle parameters of *trans* acrylic acid planar structure and comparison with structure of acryloyl chloride

Acrylic acid		Relative error (%) from the length of the same type of bond of acryloyl chloride		Acrylic acid		Relative error (%) from the value of bond angle of acryloyl chloride	
Bond	Values (Å)	The same type of bond length values of acryloyl chloride	Relative error (%)	Angle	Values (degrees)	The same type of bond angle values of acryloyl chloride	Relative error (%)
$C_1 – C_4$	1.341	1.341	0.00	$O_7C_6O_8$	122.43	N/A	N/A
$C_4 – C_6$	1.480	1.475	0.34	$C_4C_6O_8$	113.52	N/A	N/A
$C_6 – O_7$	1.220	1.198	1.84	$C_4C_6O_7$	124.04	125.40	1.08
$C_6 – O_8$	1.369	N/A	N/A	$C_4C_1H_2$	121.31	121.72	0.34
$C_1 – H_3$	1.092	1.092	0.00	$H_2C_1H_3$	117.69	117.81	0.10
$C_1 – H_2$	1.092	1.091	0.09	$H_3C_1C_4$	120.99	120.47	0.43
$C_4 – H_5$	1.092	1.094	0.18	$C_1C_4C_6$	124.57	126.21	1.30
$O_8 – H_9$	0.978	N/A	N/A	$C_6C_4H_5$	113.54	112.29	1.11
				$C_1C_4H_5$	121.89	121.49	0.33
				$C_6O_8H_9$	105.59	N/A	N/A

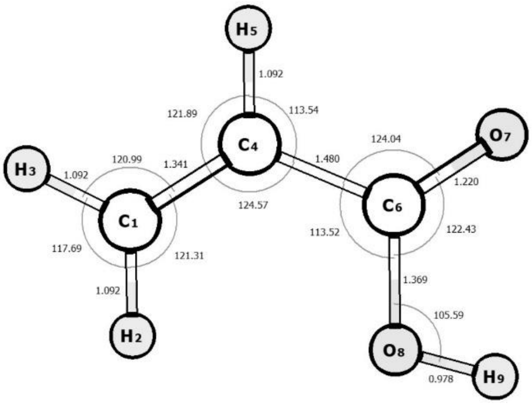


Figure 8. – The second planar structures of *trans* acrylic acid are determined by DFT/PBEPBE method with using 6-311G++(d,p) basis set

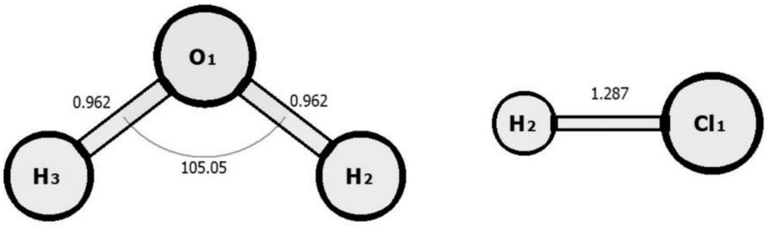
Comparing with optimized structure of acryloyl chloride, bond length and bond angle parameters of acrylic acid are similar to bond length and bond angle parameters of acryloyl chloride in group atoms (including C_1, C_4, C_6, H_2, H_3, H_5, O_7). In which, minimum relative error of bond length is 0,00 % ($C_1 – C_4$ bond and $C_1 – H_3$ bond) and maximum relative error of bond length is 1,84 % ($C_6 – O_7$ bond). That is caused by the location of these bond relative to OH substituent in acrylic acid molecule. $C_1 – C_4$ bond and $C_1 – H_3$ bond are farther from OH substituent than $C_6 – O_7$ bond. So, OH substituent affects $C_6 – O_7$ bond more than other bond in acrylic acid molecule. This influence is due to many reasons, and they will be explored in another study. With the same reasons, 0.10 % is the minimum relative error of H2C1H3 bond angle and the maximum relative error is 1.30 % ($C_1C_4C_6$).

With water and hydrogen chloride, in early studies, DFT/B3LYP method is confirmed to be a suitable method for determining optimized geometry at vapor phase [18–22]. Chosen basis set in all cases is 6-311G++(d,p). So, in this study, DFT/B3LYP/6-311G++(d,p) method is chosen for optimized geometry calculations of water and hydrogen chloride structure at vapor phase. Optimized geometry parameters of water structure and hydrogen chloride structure are also shown in Figure 9 and Table 7.

Table 7. – Optimized geometry parameters of water and hydrogen chloride structure

Compound	Bond (Å)	DFT/B3LYP	Exp	Relative error (%)	Angle (degrees)	DFT/B3LYP	Exp	Relative error (%)
Water	$O_1 – H_2$	0.962	0.958[a, b]	0.42%	H3O1H2	105.05	104.48[a, b]	0,55%
	$O_1 – H_3$	0.962	0.958[a]	0.42%	-	-	-	-
Hydrogen chloride	$Cl_1 – H_2$	1.287	1.275[c]	0.94%	N/A			

Note. [a] Experimental results from Cook et al. [27] and the references therein.
[b] Experimental results from Hoy et al. [28] and the references therein.
[c] Experimental results from Hehre et al. [29] and the references therein.



(a) H_2O structure (b) HCl structure

Figure 9. Structures of water and hydrogen chloride

Optimized geometry parameters of water and hydrogen chloride structure is calculated by DFT/B3LYP/6-311G++(d,p) method which are very small relative errors with comparing to experimental, about under 1 %. With these relative errors, DFT/B3LYP/6-311G++(d,p) method is reliable enough to be used to calculate the thermodynamic parameters of water and hydrogen chloride.

3.5. Calculation results of thermodynamic properties water, acetic acid and hydrogen chloride

Thermodynamic properties of water, hydrogen chloride, and acrylic acid at vapor phase in temperature range from 298.15 to 1000.00 K in steps of 100.00 K are determined by DFT/B3LYP/6-311G++(d,p) which are shown in Table 8, 9, and thermodynamic properties values acrylic acid are determined by DFT/PBEPBE/6-311G++(d,p) which are shown at Table 10. Thermodynamic properties are determined as entropy (S), heat capacity at constant pressure (C_P), sum of electronic and thermal enthalpies ($E_{tot} + H_{cor}$), sum of electronic and thermal free energies ($E_{tot} + G_{cor}$). Calculated entropy values and heat capacity at constant pressure values are compared with experimental values.

Table 8. Thermodynamic properties of water at vapor phase

T (K)	DFT/B3LYP/6-311G++(d,p)				Experimentation [30; 31]		Relative error (%)	
	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	$E_{tot} + H_{cor}$ (Hartree)	$E_{tot} + G_{cor}$ (Hartree)	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	S	C_P
298.15	188.73	33.49	-76.433469	-76.454891	188.84	33.60	–	–
300.00	188.93	33.50	-76.433445	-76.455024	–	–	–	–
400.00	198.65	34.14	-76.432159	-76.462410	–	–	–	–
500.00	206.37	35.09	-76.430841	-76.470125	–	35.22	–	–
600.00	212.86	36.15	-76.429485	-76.478109	–	36.31	–	–
700.00	218.52	37.25	-76.428088	-76.486323	–	37.48	–	–
800.00	223.56	38.38	-76.426648	-76.494740	–	38.74	–	–
900.00	228.15	39.53	-76.425165	-76.503340	–	39.99	–	–
1000.0	232.38	40.70	-76.423637	-76.512107	–	41.32	–	–

Table 9. Thermodynamic properties of hydrogen chloride at vapor phase

T (K)	DFT/B3LYP/6-311G++(d,p)				Experimentation [30; 31]		Relative error (%)	
	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	$E_{tot} + H_{cor}$ (Hartree)	$E_{tot} + G_{cor}$ (Hartree)	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	S	C_P
298.15	186.71	29.11	-460.824042	-460.845235	186.90	29.14	0.1	0.1
300.00	186.89	29.11	-460.824022	-460.845367	–	–	–	–
400.00	195.26	29.13	-460.822913	-460.852649	–	–	–	–
500.00	201.78	29.24	-460.821802	-460.860212	–	–	–	–
600.00	207.13	29.48	-460.820685	-460.867998	–	–	–	–
700.00	211.70	29.85	-460.819556	-460.875973	–	–	–	–
800.00	215.71	30.31	-460.818411	-460.884110	–	–	–	–
900.00	219.31	30.83	-460.817247	-460.892393	–	–	–	–
1000.0	222.59	31.36	-460.816063	-460.900805	–	–	–	–

Table 10. Thermodynamic properties of acrylic acid at vapor phase

T (K)	DFT/PBEPBE/6-311G++(d,p)				Experimentation [32]		Relative error (%)	
	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	$E_{tot} + H_{cor}$ (Hartree)	$E_{tot} + G_{cor}$ (Hartree)	S (J·mol^{-1}·K^{-1})	C_P (J·mol^{-1}·K^{-1})	S	C_P
298.15	301.76	81.72	-266.873162	-266.907414	–	81.8	–	0.10
300.00	302.26	82.09	-266.873104	-266.907627	–	82.18	–	0.10
400.00	328.52	100.85	-266.869612	-266.919641	–	101.24	–	0.39
500.00	352.75	116.33	-266.865467	-266.932616	–	116.65	–	0.27
600.00	375.10	128.76	-266.860793	-266.946477	–	128.73	–	0.02
700.00	395.73	138.83	-266.855692	-266.961156	–	138.32	–	0.37
800.00	414.83	147.15	-266.850244	-266.976590	–	146.12	–	0.70
900.00	432.58	154.16	-266.844504	-266.992725	–	152.60	–	1.02
1000.0	449.14	160.12	-266.838519	-267.009513	–	158.08	–	1.29

3.6. Calculation results of thermodynamic characteristics of reaction between acryloyl chloride and water

In a fire, reaction between acryloyl chloride and water occurs at vapor phase with mole ratio: $C_3H_3OCl + H_2O \rightarrow C_3H_4O_2 + HCl$ [8]. Heat of reaction and free energy of reaction are calculated by using (3) and (1). $(E_{tot} + H_{cor,T})$ and $(E_{tot} + G_{cor,T})$, previously received values of acryloyl chloride, water, hydrogen chloride and acrylic acid are used to calculate heat of reaction and free energy of reaction in temperature range from 298.15 to 1000.00 K in steps of 100.00 K at 1.0 atm pressure. They are shown in Table 9.

Table 11. Heat of reaction and free energy of reaction between acryloyl chloride and water

T (K)	Heat of reaction, (kJ·mol^{-1})	Free energy of reaction, (kJ·mol^{-1})
298.15	-359.919	-356.309
300.00	-359.930	-356.288
400.00	-360.213	-355.023
500.00	-360.266	-353.715
600.00	-360.148	-352.410
700.00	-359.898	-351.142
800.00	-359.560	-349.911
900.00	-359.142	-348.732
1000.0	-358.675	-347.600

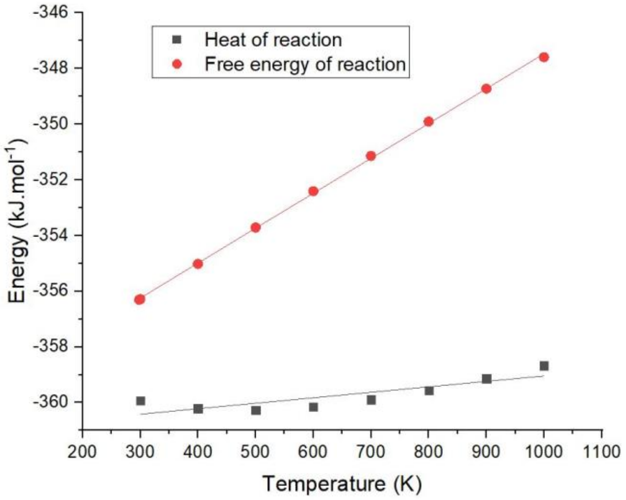


Figure 10. – The dependence of heat and free energy of reaction between acryloyl chloride and water on the temperature

The results are presented in Table 11 and Figure 10. Some comments about the reaction of acryloyl chloride with water are given below.

With heat of reaction between acryloyl chloride and water, all received values are less than 0 kJ.mol^{-1}. So, this reaction is the exothermic reaction in a fire [33]. This amount of heat is relatively large because minimum value of the heat released of the reaction is 358.675 kJ.mol^{-1} which is not much smaller than heat released of fire reaction (about 418 kJ per mole of oxygen) [34]. Heat reaction values decrease with increasing temperature in temperature range from 298.15 to 500 K and they increase with increasing temperature in temperature range from 500 to 1000 K. This variation of heat of reaction is not linear. The maximum released heat of reaction is 360.266 kJ.mol^{-1} at 500 K. This temperature point may be the point at which the reaction between acryloyl chloride and water begins to occur at a rate large enough to overcome the potential energy barrier. However, that is likely be confirmed in another study of the kinetics of this reaction.

With free energy of reaction between acryloyl chloride and water, all received values are less than 0 kJ.mol^{-1}. So, on the thermodynamic conditions reaction between acryloyl chloride and water is likely to occur at any temperature in the fire [33]. The free energy values of this reaction have a linear variation in the temperature range from 298.15 to 1000 K, in which they increase with increasing temperature.

3.7. Recommendation in fighting of the acryloyl chloride fire

In a fire which is caused by a combustion reaction of acryloyl chloride or a fire with a leak of this compound, fire-fighting has become extremely complicated because of selection of fire extinguishing agents. Water is the most common fire extinguishing agent, however, using water in this case carries many risks because of the strong reaction between acryloyl chloride and water that is reflected in the very negative free energy value of this reaction. Other hand, the heat released by this reaction can increase the danger of a fire. Therefore, water should be limited for fighting the fires of acryloyl chloride, especially water in fog form or small water jet. In small fires of acryloyl chloride, carbon dioxide, dry chemical such as sodium bicarbonate or ammonium hydrogen phosphate are extinguishing agents which are recommended for firefighting [35]. However, in large acryloyl chloride fires water can still be used in overflow form to increase efficiency in extinguishing fires if water is not in direct contact with acryloyl chloride.

4. Conclusion

With acryloyl chloride, calculating geometry optimizations of molecules and thermodynamic properties by applying DFT method shoed the good results (comparing with empirical results). The conclusions of this quantum chemical study about reaction between acryloyl chloride and water are as follows.

In a fire, reaction between acryloyl chloride and water occur in vapor phase because the boiling point of reactants and productions are less than the temperature of the fire.

Thermodynamic properties of acryloyl chloride, acrylic acid, water, and hydrogen chloride are calculated by DFT method. These calculations are based on their optimized structure.

The free energy calculation of this present study clearly indicates that according to thermodynamic conditions, reaction between acryloyl chloride and water is likely to occur at any temperature in the fire. This result is one of the scientific bases to confirm the strongly reactivity of acryloyl with water in a fire.

This reaction is the exothermic reaction in a fire. So, if firefighters use water to suppress the burning of acryloyl chloride, a large amount of heat will be released. This heat makes the fire more dangerous and difficult to fight.

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Calculation of the thermodynamic parameters of the reaction between acryloyl chloride and water by density functional theory

Расчет термодинамических параметров реакции акрилоилхлорида с водой методом теории функционала плотности

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РАСЧЕТ ТЕРМОДИНАМИЧЕСКИХ ПАРАМЕТРОВ РЕАКЦИИ АКРИЛОИЛХЛОРИДА С ВОДОЙ МЕТОДОМ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

Нгуен Хуу Хиеу, Фан Ань, Ле Ань Туан, Нгуен Тхи Нгок Ань

Цель. Исследование термодинамических свойств акрилоилхлорида для прогнозирования опасности при тушении акрилоилхлорида водой.

Методы. Термодинамические свойства (включая энтальпию, свободную энергию, энтропию и теплоемкость при постоянном давлении) акрилоилхлорида в паровой фазе при давлении 1,0 атм и диапазоне температур от 298,15 до 1000,00 K с шагом 100,00 K определялись расчетами DFT с использованием функционала PBEPBE. В качестве базисного набора использован 6-311G++(d,p).

Результаты. Рассчитаны свободная энергия и теплота реакции между акрилоилхлоридом и водой в огне (в том же диапазоне температур и давления). В диапазоне температур от 298,15 до 1000,00 K реакция между акрилоилхлоридом и водой является экзотермической. Таким образом, если пожарные используют воду для тушения возгорания акрилоилхлорида, то будет выделяться большое количество тепла. Это тепло делает огонь более опасным и трудным для борьбы.

Область применения исследований. Результаты исследований могут быть использованы при прогнозировании опасности возгорания акрилоилхлорида и способов его тушения.

Ключевые слова: горение акрилоилхлорида, реакция с водой, термодинамические свойства, DFT, акрилоилхлорид, тушение водой.

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