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QUANTUM-CHEMICAL MODELLING OF THE QUANTITATIVE PARAMETERS THAT DETERMINE THE FIRE SAFETY OF THE ANILINE IN BOUND STATE WITH COPPER(II) CHLORIDE

The crystals of the $[Cu(C_6H_5NH_2)_2Cl_2]$ complex have been prepared by direct interaction of the aniline with copper(II) chloride and the flash point and ignition temperature was measured for them. Based on the data about crystal structure of this complex the quantum-chemical analysis of ability of the copper salts to decrease combustibility of the amines was carried out. The computes showed that chemical bonding of the nonflammable copper(II) chloride with the combustible aniline (the Cu(II)–N bonding energy is 169 kJ/mol) leads almost to the double decrease of calorific capacity of the amine in bound state (the lower calorific capacity of $[Cu(C_6H_5NH_2)_2Cl_2]$ is 18625.3 kJ/kg). All this is well coordinated with the obtained data about flash point and ignition temperature which were determined for aniline in a free and bound state.

Keywords: *aniline, amine combustibility, coper(II) chloride, quantum-chemistry, thermo-chemistry, flash point and ignition temperature.*

Introduction. Systematic search of the novel chemical agents which are able efficiently to decrease a combustibility of the various organic compounds widely used in the chemical industry [1] there are one of the most actual problems of the fire safety [2]. So, the aniline belonging to a family of the nitrogen-containing hydrocarbons is industrially important organic compound and this substance is very flammable. Some physical-chemical and combustible properties of aniline are $t_{melting}$ = –5.96°C, $t_{boiling}$ = 184.4°C, t_{flash} = 73°C, $t_{ignition}$ = 76°C, $t_{autoignition}$ = 493°C, $\Delta H^{\circ}_{formation}$ = 31.1 kJ/mol and $\Delta H^{\circ}_{combustion}$ = –3392.15 kJ/mol. The mixture of aniline vapour with air is highly explosive (the minimal dangerously explosive content of oxygen (φ, %) is 13.8) [3, 4]. Among the perspective chemical agents the inorganic cupric salts are able effectively to decrease combustibility of the nitrogen-containing hydrocarbons [5, 6].

Earlier the chemical influence of the copper(I) chloride on burning of the aniline was studied in the Aniline–Air–CuCl–HCl–H_2O reacting system [7, 8]. It was shown that the effective inhibition of burning of the aniline by the hydrochloride aqueous solution of the copper(I) chloride is caused by the strong $H^+\leftarrow$N bonding (that is, by the protonation of amines at the time of a complexation) [9]. To continue research, we undertook the experimental and quantum-chemical study of interaction of the aniline with the copper(II) chloride and the thermo-chemical calculations of change of a energy state of the aniline occurring in the Aniline–Air–$CuCl_2$–H_2O reacting system.

The work purpose were to prepare the crystals of the $[Cu(C_6H_5NH_2)_2Cl_2]$ complex, to measure their of flash point and ignition temperature, to compute by means of quantum chemistry the bonding energy in the complex and, in this way, to estimate the calorific capacity of aniline in a free and bound state.

Experimental section. *Preparation of $[Cu(C_6H_5NH_2)_2Cl_2]$*. Black-violet crystals of the $[Cu(C_6H_5NH_2)_2Cl_2]$ complex were obtained by direct interaction of aniline with copper(II) chloride. The aqueous solution of $CuCl_2 \cdot H_2O$ (17 g, 0.01 mol) has been prepared at ~90°C whereupon the aniline (18.6 g, 0.02 mol) was added. At the same time the initially deep-green colour of the solution changed on the black-blue. Slow cooling to room temperature gave black-violet crystals of $[Cu(C_6H_5NH_2)_2Cl_2]$ complex.

Determination of the flash point and ignition temperature. The obtained crystals were separated from solution and were dried on air at ~70°C. The crystals were powdered in a porcelain mortar directly before tests. The flash point and ignition temperature were measured in an open crucible on three samples weighing 3 g each in accordance with an all-Union State Standard 12.1.044-89 technique [10]. Results of the made experiment are given in Table 1.

Table 1

Measurement results of the flash point and ignition temperature for crystals of the [Cu($C_6H_5NH_2$)$_2$$Cl_2$] complex

Test temperature,°C	Observed effects
80	melting
167.4	flash
195.7	ignition

Quantum-chemical computation. Numerical modelling of electronic structure of the [Cu($C_6H_5NH_2$)$_2$$Cl_2$] complex was performed by quantum chemistry method (the HyperChem professional version 6,03 program [11]) with using a semi-empirical approach ZINDO/1 [12]. At first the isolated fragment (Fig.) is generated starting from data about crystal structure of [Cu($C_6H_5NH_2$)$_2$$Cl_2$] compound. Computations were carried out for vaporous state of the [Cu($C_6H_5NH_2$)$_2$$Cl_2$] molecule without optimization of the fragment. Integral energy of all chemical bonds in the [Cu($C_6H_5NH_2$)$_2$$Cl_2$] fragment as well as in the optimized molecule of aniline was found (Table 2). Furthermore the results of quantum-chemical computation of chemical bonds energy and it known data about formation enthalpy of some elementary substances and chemical compounds at vaporous state also are presented in the Table 2 [13, 14].

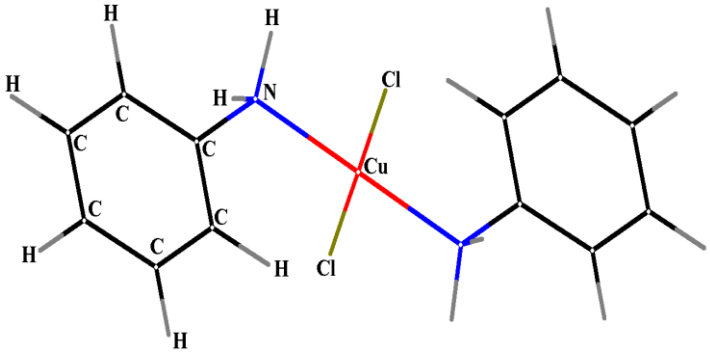

Fig. *The [Cu($C_6H_5NH_2$)$_2$$Cl_2$] isolated fragment.*

Thermo-chemical analysis. Combustibility of the investigated substances was assessed on basis of the enthalpy and the calorific capacity [14] with applying Hess's law [15]. So, formation of a molecule of aniline (*an*) in standard conditions is performed at two stages, starting from graphite, molecular hydrogen and nitrogen.

Stage 1. 6C(graphite) = 6C(g), $\Delta H_1^\circ = 6E_{\text{atomization (graphite)}}$ (kJ)

Stage 2. 6C(g) + 3,5H_2(g) + 0,5N_2(g) = $C_6H_5NH_2$(g), $\Delta H_2^\circ = 3{,}5E_{\text{H–H}} + 0{,}5E_{\text{N≡N}} - \Sigma E_{\text{chemical bonds (}an\text{)}}$ (kJ)

Then we determine the standard formation enthalpy of the gaseous aniline ($\Delta Í^\circ_{\text{formation an (g)}}$).

$$\Delta Í^\circ_{\text{formation } an\text{ (g)}} = \Delta H_1^\circ + \Delta H_2^\circ = (6E_{\text{atomization (graphite)}} + 3{,}5E_{\text{H–H}} + 0{,}5E_{\text{N≡N}}) - \Sigma E_{\text{chemical bonds (}an\text{)}} = +20.28 \text{ kJ/mol}$$

The value of $\Delta Í^\circ_{\text{formation } an\text{ (g)}}$ gives a chance to put into practice the thermo-chemical computation of full combustion of gaseous aniline in air. The equation for this reaction may be represented as

$C_6H_5NH_2$(g) + 7,75(O_2(g) + 3,76N_2(g)) = 6CO_2(g) + 3,5H_2O(g) + 29,64N_2(g), $\Delta Í^\circ_{\text{lower combustion } an\text{ (g)}}$

Table 2

Integral energy of all chemical bonds and formation enthalpy in the molecules of [Cu($C_6H_5NH_2$)$_2$$Cl_2$], aniline, some elementary substances and chemical compounds

No.	Gaseous molecules	$\Sigma E_{\text{chemical bonds}}$, kJ/mol	$\Delta Í^{\circ}_{\text{formation}}$, kJ/mol
1	$[Cu(C_6H_5NH_2)_2Cl_2]$	13150.2	—
2	$C_6H_5NH_2$	6282.8	—
3	C(graphite)→C(g)	—	+717.7
4	Cl–Cl	242.36	0
5	H–H	435.57	0
6	N≡N	944.68	0
7	H–Cl	427.0	–92.2
8	CO_2	—	–393.1
9	H_2O	—	–241.6
11	Cu^{II}–Cl in Cu_2Cl_4	193.2	–222.3
12	CuO	—	+310.0

The calculated lower standard combustion enthalpy of the aniline is –3224.48 kJ/mol while the converting on the 1 kg of the substance (i.e. calorific capacity $Q_{\text{lower combustion } an\,(g)}$) gives +34671.83 kJ/kg.

In the same way the standard formation enthalpy for the vaporous isolated fragment ($[Cu(an)_2Cl_2]$) is calculated, starting from gaseous Cu_2Cl_4 and aniline (reaction 3).

Reaction 3. $1/2Cu_2Cl_4(g) + 2C_6H_5NH_2(g) = [Cu(C_6H_5NH_2)_2Cl_2](g)$, ΔH°_3

Taking into account the energy of the Cu–Cl bond which was calculated for the Cu_2Cl_4 molecular particle predominant in the vaporous copper(II) chloride as well as the integral energy of the chemical bonds in the molecules of aniline and $[Cu(an)_2Cl_2]$ (see Table 2) the ΔH°_3 was determined.

$$\Delta H^{\circ}_3 = (6/2E_{\text{Cu–Cl}} + 2\Sigma E_{\text{chemical bonds }(an)}) - \Sigma E_{\text{chemical bonds}}([Cu(an)_2Cl_2]) = -5.0 \text{ kJ}$$

Then

$$\Delta Í^{\circ}_{\text{formation}}[Cu(an)_2Cl_2]\,(g) = \Delta H^{\circ}_3 + 1/2\,\Delta Í^{\circ}_{\text{formation}}\,Cu_2Cl_4\,(g) + 2\,\Delta Í^{\circ}_{\text{formation}}\,an\,(g) = -100.1 \text{ kJ/mol}$$

Herefrom the thermo-chemical computation of full combustion of $[Cu(an)_2Cl_2]$ gaseous molecules in air was carried out using the reaction equation.

$$[Cu(C_6H_5NH_2)_2Cl_2](g) + 14.5(O_2(g) + 3.76N_2(g)) =$$

$$= 12CO_2(g) + 6H_2O(g) + CuO(g) + 2HCl(g) + 55.52N_2(g),\ \Delta Í^{\circ}_{\text{lower combustion}}[Cu(an)_2Cl_2]\,(g)$$

Thus based on known values of the standard formation enthalpy for the CO_2, H_2O, HCl and CuO gaseous molecules (see Table 2) the calculated lower standard combustion enthalpy and calorific capacity of the $[Cu(an)_2Cl_2]$ are –6046.8 kJ/mol and +18896,2 kJ/kg for $\Delta Í^{\circ}_{\text{lower combustion}}[Cu(an)_2Cl_2]\,(g)$ and $Q_{\text{lower combustion}}[Cu(an)_2Cl_2]\,(g)$ respectively.

Results and discussion. The study of the complexation occurring in the Air–Aniline–$CuCl_2$–H_2O system showed that bonding uninflammable $CuCl_2$ salt with inflammable aniline leads to formation of the practically slow-inflammable $[Cu(an)_2Cl_2]$ compound. All this is accompanied by calorification about 340 kJ on each formula unit of the complex. Such effect is achieved mainly by overlap of the $2p_z$-orbital containing unshared electron pair of the nitrogen atom with unoccupied hybrid sp^3d^2-orbital of the copper atom. The donor-acceptor Cu^{2+}←N bond is so formed.

All this corroborates once again that energy of donor-acceptor interaction is able significantly to decrease combustible properties of aniline. Such influence of change of an energy state of aniline at the time of a complexation on its combustibility is well correlated with experimental and calculated data. So, the thermo-chemical calculations showed that calorific capacity of the vaporous $[Cu(C_6H_5NH_2)_2Cl_2]$ complex relatively of the same of the gaseous aniline molecule decreases almost twice. Experimental determination of the flash point and ignition temperature the performed

for crystals of the complex shows that aniline in the bound state as a matter of fact becomes non-flammable. So, the flash point of the aniline afterward bonding with $CuCl_2$ increases from 73°C to 167.4°C and the ignition temperature does from 76°C to 195.7°C respectively. The reason of this is additional chemical bonds which are forming between inflammable aniline and an inorganic component part of a complex. For break of these bonds a some quantity of heat needs to be used up. The effect of inhibition of burning organic amines by salts of the copper(II) exactly in this consists.

Conclusions. Thus the processes of a complexation studied on the example of interaction of the aniline with $CuCl_2$, successfully can be used for increase of fire safety of various chemical industries. In particular, this is for storing, transportation and deactivation of the nitrogen-containing hydrocarbons participating in chemical production cycles. On the other hand the inorganic salts of copper (in particular copper(II) chloride) can be applied at elaboration of the fire-retardant composite materials for the synthetic polymers, amino-epoxy resins etc. as well as at making the fire-extinguishing aerosols for efficient suppression of a hydrocarbonic flame and the foamy fire-extinguishing means.

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КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ КІЛЬКІСНИХ ПАРАМЕТРІВ ПОЖЕЖО-ВИБУХОНЕБЕЗПЕКИ АНІЛІНУ У ЗВ'ЯЗАНОМУ З КУПРУМ(II) ХЛОРИДОМ СТАНІ

Кристали комплексу $[Cu(C_6H_5NH_2)_2Cl_2]$ були отримані прямою взаємодією аніліну з купрум(II) хлоридом, для яких визначені температури спалаху та займання. Базуючись на відомостях про кристалічну структуру комплексу $[Cu(C_6H_5NH_2)_2Cl_2]$ здійснено квантово-хімічний аналіз спроможності солей купруму знижувати горючість амінів. Обчислення засвідчили, що хімічне зв'язування негорючого купрум(II) хлориду з горючим аніліном ($E_{зв'язку}$ Cu(II)–N 169 кДж/моль) зумовлює майже двократне зниження теплотворної спроможності аміну у зв'язаному стані ($Q_{н.згор.}[Cu(C_6H_5NH_2)_2Cl_2]$ 18625,3 кДж/кг). Це добре узгоджується з результатами експериментального визначення температур спалаху і займання, проведеного для зв'язаного в кристалічний комплекс та вільного аніліну.
Ключові слова: *анілін, горючість амінів, купрум(II) хлорид, квантово-хімічні обчислення, термохімія, температури спалаху і займання.*

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КВАНТОВО-ХИМИЧЕСКОЕ МОДЕЛЛИРОВАНИЕ КОЛИЧЕСТВЕННЫХ ПАРАМЕТРОВ ПОЖАРОВЗРЫВООПАСНОСТИ АНИЛИНА В СВЯЗАННОМ С ХЛОРИДОМ МЕДИ(II) СОСТОЯНИИ

Кристаллы комплекса $[Cu(C_6H_5NH_2)_2Cl_2]$ были получены прямым взаимодействием анилина с хлоридом меди(II), для которых определены температуры вспышки и воспламенения. Основываясь на сведениях о кристаллической структуре комплекса $[Cu(C_6H_5NH_2)_2Cl_2]$ осуществлен квантово-химический анализ способности солей меди снижать горючесть аминов. Расчеты показали, что химическое связывание негорючего хлорида меди(II) с горючим анилином ($E_{связи}$ Cu(II)–N 169 кДж/моль) обусловливает почти двукратное снижение теплотворной способности амина в связанном состоянии ($Q_{н.сгор.}[Cu(C_6H_5NH_2)_2Cl_2]$ 18625,3 кДж/кг). Это хорошо согласуется с результатами экспериментального определения температур вспышки и воспламенения, проведенного для связанного в кристаллический комплекс и свободного анилина.
Ключевые слова: *анилин, горючесть аминов, хлорид меди(II), квантово-химические расчеты, термохимия, температуры вспышки и воспламенения.*