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Quantum chemical approach to calculating the enthalpies of the formation of alkali metal xanthates

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Objectives. *The aim of this work is to study the possibility of the joint use of quantum chemical methods and correlation analysis to determine the formation enthalpies of metal-containing organic substances using the example of alkali metal xanthates, which are of interest as biologically active substances and effective flotation reagents.*
Methods. *Semi-empirical methods of quantum chemical calculating (Modified Neglect of Diatomic Overlap, Austin Model 1, Recife model 1 methods) and linear regression analysis were used.*
Results. *Using the semi-empirical Modified Neglect of Diatomic Overlap, Austin Model 1, and Recife model 1 methods, the enthalpies of formation of 16 potassium and sodium alkyl xanthates were calculated, and the obtained results were compared with experimental data. It was found that the best correlation for potassium and sodium salts of dithiocarbonic acid esters could be observed using the Austin Model 1 method. Using the obtained regression equations, the enthalpies of formation were calculated for 30 xanthates, the organic part of which contained alkyl, cyclic non-aromatic structures, and one or two heteroatoms such as nitrogen, oxygen, and fluorine, and for which there are no experimental data.*
Conclusions. *As a result of the study, an excellent correlation was established between the experimental and the calculated (by the Austin Model 1 method) values of the enthalpies of formation of potassium and sodium alkyl xanthates. The data obtained can be used to calculate the thermal effect of the xanthogenation reactions of alcohols and to design the production of the corresponding xanthates.*

Keywords: *alkali metal xanthates, semi-empirical quantum chemical calculation methods, correlation analysis, formation enthalpy.*

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Квантово-химический подход к расчету энтальпий образования ксантогенатов щелочных металлов

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Цели. *Целью работы является исследование возможности совместного использования квантово-химических методов и корреляционного анализа для определения энтальпий образования металлосодержащих органических веществ на примере ксантогенатов щелочных металлов, которые представляют интерес как биологически активные вещества и эффективные флотореагенты.*
Методы. *Использованы полуэмпирические методы квантово-химических расчетов Modified Neglect of Diatomic Overlap, Austin Model 1, Recife model 1 и линейный регрессионный анализ.*
Результаты. *С помощью полуэмпирических методов Modified Neglect of Diatomic Overlap, Austin Model 1, Recife model 1 вычислены энтальпии образования 16 алкилксантогенатов калия и натрия, проведено сопоставление полученных результатов с экспериментальными данными. Выяснено, что наилучшая корреляция для калиевых и натриевых солей эфиров дитиоугольной кислоты наблюдается при использовании метода Austin Model 1. С помощью полученных уравнений регрессии вычислены энтальпии образования для 30 ксантогенатов, органическая часть которых содержит алкильные, циклические неароматические структуры и один или два гетероатома, такие как N, O, F, и экспериментальные данные по которым отсутствуют.*
Выводы. *В результате проведенного исследования была установлена превосходная корреляция между экспериментальными и рассчитанными по методу AM1 значениями энтальпий образования алкилксантогенатов калия и натрия. Полученные данные могут быть использованы для расчета теплового эффекта реакций ксантогенирования спиртов и проектирования производств соответствующих ксантогенатов.*

Ключевые слова: *ксантогенаты щелочных металлов, полуэмпирические квантово-химические методы расчета, корреляционный анализ, энтальпия образования.*

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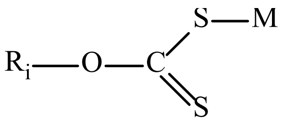
INTRODUCTION

The thermodynamic characteristics of a substance are its most important parameters. Thermodynamic analysis of a chemical process allows one to determine the direction of the reaction, the equilibrium conditions, and the thermal effect of the process. However, the task of determining the thermodynamic characteristics, primarily, the enthalpies of formation of various organic substances, is time-consuming, and for some compounds, it is not feasible at all. Due to the development of quantum chemistry and computer technology, the thermodynamic parameters of many compounds can now be quickly calculated using various methods; however, it is not possible to fully rely on the obtained values, and it is always necessary to verify the results of calculations with experimental data. Earlier studies, using a combination of semi-empirical quantum chemical methods of calculation and correlation analysis, determined the enthalpies of formation of many organic compounds, for example: cyclophanes [1]; nitrogen-containing heterocycles [2]; and derivatives of adamantane [3]. For the calculations, compounds were used that included the most frequently found elements in organic chemistry: carbon, hydrogen, oxygen, nitrogen, and sulfur. At present, many other organic substances are widely used in the national economy, which, in addition to the elements listed above, also include various metals. Calculating the thermodynamic characteristics of these types of substances is challenging. Therefore, research into the possibility of combining quantum chemical methods and correlation analysis to find the formation enthalpies of such compounds is urgently needed.

MATERIALS AND METHODS

As representatives of the studied group of substances, the salts of dithiocarbonic acid O-esters (xanthates of alkali metals) were chosen, represented by the general formula:



where R_i is the organic part of the molecule, M = Na, K. These compounds are widely used as flotation-reagent collectors [4], and also have a pronounced biological activity [5, 6]. The numbering and structure of xanthates are presented in Table 1.

To identify the correlation between the calculated and experimental values of the enthalpy of formation, 16 compounds were selected: methyl (I, II), ethyl (III, IV), isopropyl (V, VI), propyl (VII, VIII), butyl (IX, X), amyl (XI, XII), hexyl (XIII, XIV) and heptyl (XV, XVI) potassium and sodium xanthates (odd numbers correspond to potassium xanthates, even numbers to sodium). The literature [7–11] contains experimental data on the thermal effect of the xanthogenation reactions of the corresponding alcohols ($\Delta H^0_{\text{r, 298}}$):

$$ROH + CS_2 + KOH \rightarrow ROC(S)SK + H_2O.$$

The formation enthalpies of substances I–XVI ($\Delta H^0_{\text{f, exp.}}$) were determined using reference data on the participants' enthalpies of formation in the reaction and Hess's law. For these compounds, geometry optimization and calculation of formation enthalpies were also performed using the Modified Neglect of Diatomic Overlap (MNDO), Austin Model 1 (AM1), and Recife Model 1 (RM1) methods in the HyperChem software package. The calculation results are presented in Table 2.

Table 1. List of investigated potassium and sodium xanthates (odd numbers correspond to potassium xanthates, even numbers correspond to sodium xanthates)

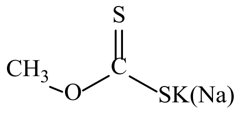
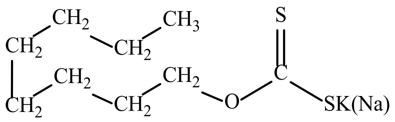
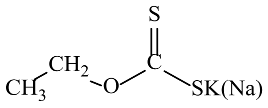
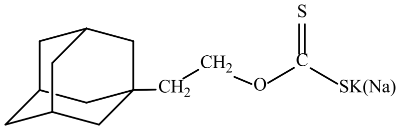
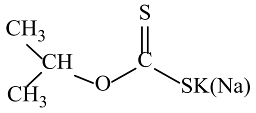
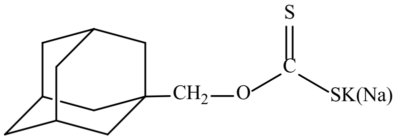
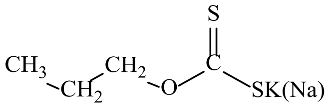
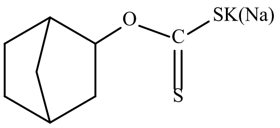
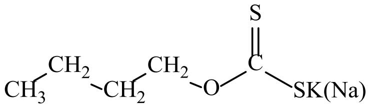
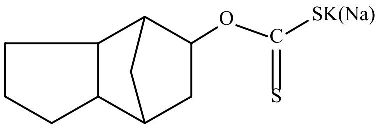
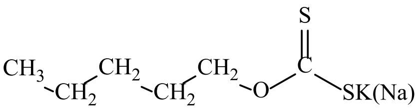
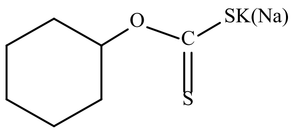
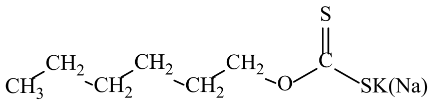
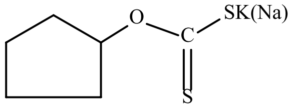
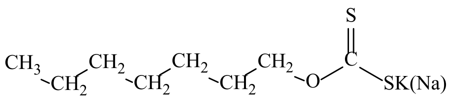
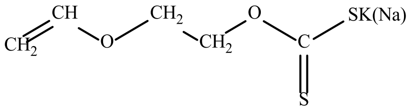
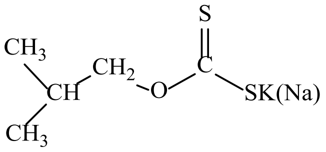
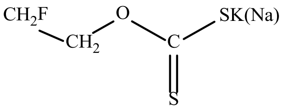
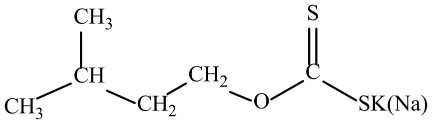
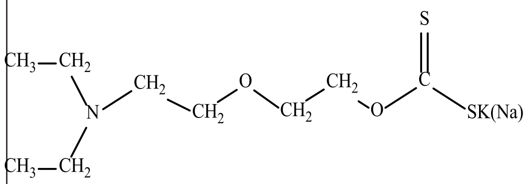
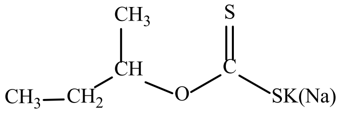
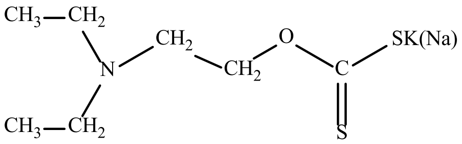
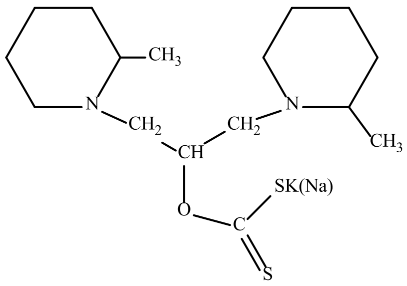
No.	Compound	No.	Compound
I, II		XXIII, XXIV	
III, IV		XXV, XXVI	
V, VI		XXVII, XXVIII	
VII, VIII		XXIX, XXX	
IX, X		XXXI, XXXII	
XI, XII		XXXIII, XXXIV	

Table 1. Continued

No.	Compound	No.	Compound
XIII, XIV		XXXV, XXXVI	
XV, XVI		XXXVII, XXXVIII	
XVII, XVIII		XXXIX, XL	
XIX, XX		XLI, XLII	
XXI, XXII		XLIII, XLIV	
XLV, XLVI			

It was found that a general linear correlation was absent; however, the experimental and calculated data fitted on a straight line separately for potassium and sodium xanthates. Moreover, for each of the calculation methods, the correlation coefficients for the group of sodium xanthates were slightly higher than for the group of potassium xanthates. The highest correlation coefficient in both cases was characteristic of the AM1 method in which r > 0.99, which indicates excellent correlation. The regression equations in this case are:

$$\Delta H^0_{\text{f, exp., K}} = 0.8736 \times \Delta H^0_{\text{f, calc., K}} - 92.2980 \qquad (1)$$

$$\Delta H^0_{\text{f, exp., Na}} = 0.8738 \times \Delta H^0_{\text{f, calc., Na}} - 124.0000 \qquad (2)$$

The obtained dependencies can be used to find the formation enthalpy of those potassium and sodium xanthates, experimental data for which are not available in scientific and technical literature. For further calculations, potassium (odd numbers) and sodium (even numbers) xanthates were selected based on the following alcohols: 2-methylpropan-1-ol (XVII, XVIII), 3-methylbutan-1-ol (XIX, XX), butan-2-ol (XXI, XXII), octan-1-ol (XXIII, XXIV), (1-adamantyl) methanol (XXV, XXVI), 2-(1-adamantyl)-ethan-1-ol (XXVII, XXVIII), bicyclo-[2.2.1]-heptan-2-ol (XXIX, XXX), 2-(vinyloxy)-ethan-1-ol (XXXI, XXXII), 2-fluoroethan-1-ol (XXXIII, XXXIV), 2-(*N,N*-diethylamino)-ethan-1-ol (XXXV, XXXVI), 2-(*N,N*-diethylaminoethoxy)-ethan-1-ol (XXXVII, XXXVIII), cyclopentanol (XXXIX, XL), cyclohexanol (XLI, XLII), 1,3-di-(2-methylpiperidino)-propan-2-ol (XLIII, XLIV), and tricyclo-[5.2.1.0]-decan-9-ol (XLV, XLVI). All these substances are described in the literature [6, 12–19] and are either highly efficient flotation reagents-collectors or exhibit high biological activity.

The results of the calculation of the above xanthates by the AM1 method, and subsequent recalculation of the formation enthalpies according to the regression equations (1) and (2), are given in Table 3.

Table 2. Data of quantum-chemical calculation of formation enthalpy $\Delta H^0_{\text{f, calc.}}$ performed by MNDO, AM1, RM1 methods for xanthates I-XVI and correlation coefficients

No.	$\Delta H^0_{\text{r, 298}}$ **kJ/mol**	$\Delta H^0_{\text{f, exp.}}$ **kJ/mol**	$\Delta H^0_{\text{f, calc.}}$**, kJ/mol**					
			MNDO	**Δ**	**AM1**	**Δ**	**RM1**	**Δ**
I	–45.10	–312.31	–376.94	–64.63	–259.89	52.42	–231.55	80.76
II	–28.35	–297.19	–324.9	–27.71	–210.57	86.62	–175.56	121.63
III	–47.20	–348.21	–399.41	–51.2	–284.41	63.8	–256.46	91.75
IV	–32.79	–335.43	–345.92	–10.49	–235.15	100.28	–200.5	134.93
V	–6.50	–345.3	–405.33	–60.03	–299.78	45.52	–285.9	59.4
VI	–4.97	–345.4	–346.01	–0.61	–250.42	94.98	–230.76	114.64
VII	–52.80	–376.54	–419.27	–42.73	–310.46	66.08	–277.5	99.04
VIII	–36.20	–361.57	–361.57	0	–261.2	100.37	–220.48	141.09
IX	–43.50	–384.14	–438.96	–54.82	–335.14	49	–297.7	86.44
X	–30.92	–373.19	–380.05	–6.86	–289.69	83.5	–241.14	132.05
XI	–35.40	–403.99	–455.74	–51.75	–360.26	43.73	–319.04	84.95
XII	–27.50	–397.72	–396.82	0.9	–315.15	82.57	–259.29	138.43
XIII	–32.20	–428.69	–475.2	–46.51	–384.39	44.3	–337.92	90.77
XIV	–26.10	–424.22	–417.16	7.06	–343.76	80.46	–279.53	144.69
XV	–31.80	–450.75	–494.75	–44	–411.76	38.99	–358.4	92.35
XVI	–24.54	–445.12	–433.24	11.88	–369.12	76	–296.99	148.13
Correlation coefficient			r_K = 0.9875 r_{Na} = 0.9907		r_K = 0.9907 r_{Na} = 0.9919		r_K = 0.9669 r_{Na} = 0.9841	

Table 3. Enthalpies of the formation of compounds XVII-XLVI, calculated ($\Delta H^0_{\text{f, calc.}}$) by the AM1 method and corrected ($\Delta H^0_{\text{f, calc.}}$*) by equations (1) and (2)

No.	$\Delta H^0_{\text{f, calc.}}$**, kJ/mol**	$\Delta H^0_{\text{f, calc.}}$***, kJ/mol**	**No.**	$\Delta H^0_{\text{f, calc.}}$**, kJ/mol**	$\Delta H^0_{\text{f, calc.}}$***, kJ/mol**
XVII	–328.39	–379.18	XVIII	–282.02	–370.43
XIX	–359.04	–405.96	XX	–309.78	–394.69
XXI	–325.57	–376.72	XXII	–268.17	–358.33
XXIII	–452.03	–487.19	XXIV	–403.36	–476.46
XXV	–420.30	–459.47	XXVI	–371.44	–448.56
XXVII	–401.41	–442.97	XXVIII	–342.18	–423.00
XXIX	–259.93	–319.37	XXX	–209.58	–307.13

Table 3. Continued

No.	$\Delta H^0_{\text{f, calc.}}$, kJ/mol	$\Delta H^0_{\text{f, calc.}}$*, kJ/mol	No.	$\Delta H^0_{\text{f, calc.}}$, kJ/mol	$\Delta H^0_{\text{f, calc.}}$*, kJ/mol
XXXI	–265.90	–324.59	XXXII	–242.03	–335.49
XXXIII	–359.40	–406.27	XXXIV	–304.94	–390.46
XXXV	–320.61	–372.38	XXXVI	–271.13	–360.91
XXXVII	–335.89	–385.73	XXXVIII	–285.98	–373.89
XXXIX	–484.10	–515.21	XL	–434.06	–503.28
XLI	–270.55	–328.65	XLII	–219.63	–315.91
XLIII	–481.88	–513.27	XLIV	–401.58	–474.90
XLV	–323.05	–374.51	XLVI	–274.31	–363.69

In compiling this list of xanthates, compounds were chosen so that their calculated formation enthalpy lay in the range from −200 to −500 kJ/mol for potassium and from −200 to −450 kJ/mol for sodium. The possibility of applying equations (1) and (2) for xanthates containing heteroatoms in an organic radical is evidenced by previous studies [e.g., 20]. When developing a method for producing potassium diethylaminoethyl xanthate, we evaluated the thermal effect of the reaction under adiabatic conditions. It was found that the change in the enthalpy of xanthogenation of diethylaminoethanol lies in the range from −30 to −45 kJ/mol. In this case, the calculation of the thermal effect of this reaction, taking into account the obtained calculated data, gave the result $\Delta H^0_{\text{r, 298}} = -29.56$ kJ/mol. Given that in reality, along with the main xanthogenation reaction, side exothermic processes occur:

$$6KOH + CS_2 \rightarrow K_2CO_3 + 2K_2S + 3H_2O$$

$$6KOH + 3CS_2 \rightarrow K_2CS_3 + 2K_2S + 3H_2O$$

the calculated value of the change in the enthalpy of diethylaminoethanol xanthogenation can be considered reliable.

CONCLUSIONS

In this work, an excellent correlation was established between the experimental and calculated (using the AM1 method) formation enthalpies of potassium and sodium alkyl xanthates. Using the obtained correlation equations, the formation enthalpies of various xanthates were calculated, the organic part of which contained alkyl, cyclic non-aromatic structures, and one or two heteroatoms such as nitrogen, oxygen, and fluorine. The data obtained can be used to calculate the thermal effect of the xanthogenation reaction of the corresponding alcohols and to design the production of these xanthates.

The authors declare no conflicts of interest.

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