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ENTHALPY OF FORMATION OF THIOPHENE DERIVATIVES

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The enthalpy of formation in the gas phase has been calculated for 21 carbonyl compounds of the thiophene series with the aid of the PM3, MINDO, AM1, and MNDO semiempirical quantum-chemical methods. Comparison of them with experimental data showed that the best linear correlation was achieved with the PM3 method. The latter in conjunction with a developed linear regression equation has been used to predict the enthalpy of formation of 22 carboxylic acids and ketones of the thiophene series.

Keywords: thiophene derivatives, semiempirical quantum-chemical methods of calculation, heat of formation.

The enthalpy of formation is one of the most important energy characteristics of compounds, data on which enables optimization of the conditions of carrying out technological processes involving them. However, the experimental determination of enthalpies of formation of organic compounds is fairly laborious and sometimes an insurmountable problem. Consequently all the calculating quantum-chemical methods, carried out with the aid of special sets of computer programs, are frequently used for predicting the energy properties of substances. However without a link with experimental data their application frequently gives ambiguous results, which are difficult to interpret.

In the present study the semiempirical quantum-chemical methods PM3, MINDO, AM1, and MNDO, forming part of the MOPAC program set, were used with the aim of predicting the enthalpies of formation of thiophene derivatives. Compounds of the thiophene series are encountered among products of plant origin, but have even more value as synthetic medicinal preparations and dyestuffs producible in industry [1].

The selection of a method of calculation originates from the need to provide the best correlation between calculated and experimental values of the enthalpies of formation of thiophene derivatives. The following compounds with known experimental enthalpies of formation in the gas phase were used for this purpose [2-13]: thiophene-2-carbaldehyde (**1**), thiophene-3-carbaldehyde (**2**), 3-methylthiophene-2-carbaldehyde (**3**), 5-methylthiophene-2-carbaldehyde (**4**), 5-ethylthiophene-2-carbaldehyde (**5**), 2-acetylthiophene (**6**), 3-acetylthiophene (**7**), 2-acetyl-3-methylthiophene (**8**), 2-acetyl-4-methylthiophene (**9**), 2-acetyl-5-methylthiophene (**10**), 3-acetyl-2,5-dimethylthiophene (**11**), thiophene-2-carboxylic acid (**12**), thiophene-3-carboxylic acid (**13**), 3-methylthiophene-2-carboxylic acid (**14**), 5-methylthiophene-2-carboxylic acid (**15**), 2-thienylacetic acid (**16**), 3-thienylacetic acid (**17**), 5-acetylthiophene-2-carboxylic acid (**18**), thiophene-2,5-dicarboxylic acid (**19**), 2-thienylacetic acid methyl ester (**20**), 3-thienylacetic acid methyl ester (**21**).

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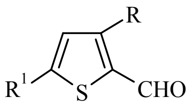
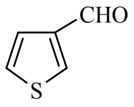


1, **3–5**



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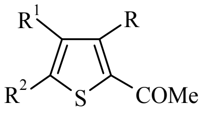
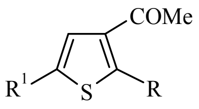
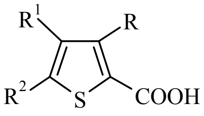


6, **8–10**

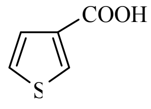


7, **11**

1 R = R^1 = H; **3** R = Me, R^1 = H; **4** R = H, R^1 = Me; **5** R = H, R^1 = Et; **6** R = R^1 = R^2 = H;
7 R = R^1 = H; **8** R = Me, R^1 = R^2 = H; **9** R = R^2 = H, R^1 = Me; **10** R = R^1 = H, R^2 = Me;
11 R = R^1 = Me



12, 14, 15, 22–32



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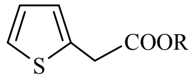

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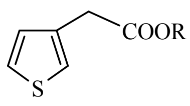
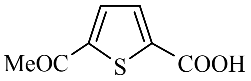


17, 21

12, **14**, **15** R^1 = H, **12** R = R^2 = H, **14** R = Me, R^2 = H, **15** R = H, R^2 = Me;
16, **17** R = H; **20**, **21** R = Me; **22** R = R^2 = H, R^1 = Me; **23**, **24** R = Me,
23 R^1 = H, R^2 = Me, **24** R^1 = Me, R^2 = H; **25** R = H, R^1 = R^2 = Me; **26** R = Et, R^1 = R^2 = H;
27 R = R^1 = H, R^2 = Et; **28–32** R = Et, **28** R^1 = H, R^2 = Me, **29** R^1 = H, R^2 = Et,
30 R^1 = Et, R^2 = H, **31** R^1 = Me, R^2 = H, **32** R^1 = R^2 = Me



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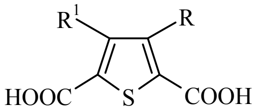
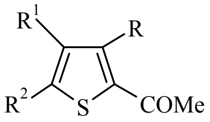


19, 33–36



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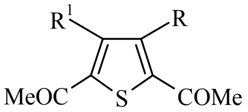

41–43

19 R = R^1 = H; **33** R = H, R^1 = Et; **34** R = R^1 = Me; **35** R = Me, R^1 = Et; **36** R = R^1 = Et;
37 R = Et, R^1 = R^2 = H; **38** R = Et, R^1 = H, R^2 = Me; **39** R = H, R^1 = Et, R^2 = Me;
40 R = Et, R^1 = R^2 = Me; **41** R = R^1 = H; **42** R = Me, R^1 = H; **43** R = R^1 = Me

For each of these compounds a complete optimization of the geometry of the molecules was carried out and their enthalpies of formation were calculated by the PM3, MINDO, AM1, and MNDO methods. The heats of formation $\Delta_f H^0_{calc}$ (Table 1), calculated by the PM3, MNDO, AM1, and MINDO methods correlate with the experimental results $\Delta_f H^0_{exp}$. The correlation coefficients were 0.9976, 0.9971, 0.9955, and 0.8022 respectively. In accordance with the system proposed by Jaffe for assessing correlation [14], the results of the calculations by the PM3, MINDO, and AM1 methods correlated in an excellent way with the experimental data for the gas phase. The best correlation link between $\Delta_f H^0_{calc}$ and $\Delta_f H^0_{exp}$ for the gas phase was provided by the use of the PM3 method. This link is described by the linear regression equation (1).

$$\Delta_f H^o_{calc} = 0.9255\ \Delta_f H^o_{exp} + 3.4049, \qquad (1)$$

TABLE 1. Data of Quantum-Chemical Calculations of Enthalpies of Formation ($\Delta_f H^0$) of Compounds **1-21** ($\Delta = |\Delta_f H^0_{calc} - \Delta_f H^0_{exp}|$)

Compound	$\Delta_f H^0_{calc}$, kJ/mol								$\Delta_f H^0_{exp}$, kJ/mol
	PM3	Δ	MINDO	Δ	AM1	Δ	MNDO	Δ	
1	-7.78	0.68	-44.03	36.93	-16.66	9.56	-32.26	25.16	-7.1±1.9 [9]
2	-14.06	6.66	-11.63	4.23	-17.92	10.52	-27.23	19.83	-7.4±1.9 [9]
3	-43.71	3.11	-72.91	32.31	-49.45	8.85	-65.52	24.92	-40.6 [6]
4	-39.68	2.38	-111.16	73.86	-49.40	12.10	-77.52	40.22	-37.3 [6]
5	-58.59	11.51	-141.48	71.38	-73.94	3.84	-98.32	28.22	-70.1 [6]
6	-37.09	22.11	-88.69	29.49	-43.64	15.56	-58.05	1.15	-59.2±2.1 [9]
7	-48.26	6.24	-51.44	3.06	-45.82	8.68	-55.53	1.03	-54.5±1.8 [9]
8	-75.56	15.34	-106.75	15.85	-69.40	21.5	-93.83	2.93	-90.9 [3]
9	-74.77	17.63	-116.79	24.39	-77.74	14.66	-99.72	7.32	-92.4 [3]
10	-66.00	30.00	-156.09	60.09	-76.57	19.43	-103.34	7.34	-96.0 [3]
11	-109.22	13. 8	-179.64	56.44	-98.66	24.54	-142.2	19.00	-123.2±2.7 [2]
12	-231.32	27.88	-324.58	65.38	-259.79	0.59	-266.75	7.55	-259.2±1.9 [7, 11]
13	-247.76	14.04	-294.21	32.41	-264.08	2.28	-266.40	4.60	-261.8±1.7 [11]
14	-267.32	28.28	—	—	-290.50	5.10	-302.79	7.19	-295.6 [3]
15	-263.14	30.66	-392.52	98.72	-292.40	1.40	-312.04	18.24	-293.8 [3]
16	-263.17	2.53	—	—	-291.47	25.77	-293.68	27.98	-265.7±2.2 [10]
17	-269.02	6.48	-293.48	17.98	-295.39	19.89	-291.05	15.55	-275.5±2.4 [10]
18	-392.68	31.62	-547.09	122.79	-412.68	11.62	-432.37	8.07	-424.3 [5]
19	-578.49	54.11	-786.74	154.14	-598.47	34.13	-639.10	6.50	-632.6±2.2 [7]
20	-230.13	38.37	—	—	-264.14	4.36	-262.51	5.99	-268.5±2.8 [13]
21	-241.87	25.73	-263.45	4.15	-267.11	0.49	-259.86	7.74	-267.6±2.4 [13]
Mean absolute deviation		18.67		49.80		12.14		13.64	

TABLE 2. Comparison of the Results of Calculating Adjusted Values of the Enthalpies of Formation in the Gas Phase ($\Delta_f H^0_{calc}$ = 0.9255, $\Delta_f H^0_{exp}$ + 3.4049; -Δ^* = $|\Delta_f H^*_{calc} - \Delta_f H_{exp}|$

Compound	Enthalpy of formation, kJ/mol			Δ^*
	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	$\Delta_f H^0_{exp}$	
1	-7.78	-12.09	-7.1 [9]	4.99
2	-14.06	-18.87	-7.4 [9]	11.47
3	-43.71	-50.91	-40.6 [6]	10.31
4	-39.68	-46.55	-37.3 [6]	9.25
5	-58.59	-66.99	-70.1 [6]	3.11
6	-37.09	-43.75	-59.2 [9]	15.45
7	-48.26	-55.82	-54.5 [9]	1.32
8	-75.56	-85.32	-90.9 [3]	5.58
9	-74.77	-84.47	-92.4 [3]	7.93
10	-66.0	-74.99	-96.0 [3]	21.01
11	-109.2	-121.69	-123.2 [2]	1.51
12	-231.32	-253.62	259.2 [7, 11]	5.58
13	-247.76	-271.38	-261.8 [11]	9.58
14	-267.32	-292.52	-295.6 [3]	3.08
15	-263.14	-288.00	-293.8 [3]	5.80
16	-263.17	-288.03	-265.7 [10]	22.33
17	-269.02	-294.35	-275.5 [10]	18.85
18	-392.68	-427.97	-424.3 [5]	3.67
19	-578.49	-628.74	-632.6 [7]	3.86
20	-230.13	-252.33	-268.5 [13]	16.17
21	-241.87	-265.02	-267.6 [13]	2.58
Mean absolute deviation				8.74

with the aid of which conversion of the calculated heats of formation of the selected compounds (Table 1) to correct them to the experimental data was carried out. The results of the conversion are given in Table 2. It is seen from the Table that on conversion of the calculated values of the heats of formation $\Delta_f H^0_{calc}$ of the selected set of compounds to the adjusted $\Delta_f H^{0*}_{calc}$ with the aid of equation (1) the deviation (denoted as Δ and Δ* respectively) from the experimentally obtained values was significantly reduced: the mean absolute deviation was 8.74 kJ/mol (in place of 18.67 kJ/mol). The greatest deviation from experimental data was observed for compounds **6**, **10**, **16**, **17**, and **20**.

The obtained linear regression equation may be used for correcting the heats of formation calculated by the PM3 method for compounds of this class. The results of such a calculation for the following thiophene derivatives with unknown experimental values of the enthalpy of formation, *viz.* 4-methylthiophene-2-carboxylic acid (**22**), 3,5-dimethylthiophene-2-carboxylic acid (**23**), 3,4-dimethylthiophene-2-carboxylic acid (**24**), 4,5-dimethylthiophene-2-carboxylic acid (**25**), 3-ethylthiophene-2-carboxylic acid (**26**), 5-ethylthiophene-2-carboxylic acid (**27**), 3-ethyl-5-methylthiophene-2-carboxylic acid (**28**), 3,5-diethylthiophene-2-carboxylic acid (**29**), 3,4-diethylthiophene-2-carboxylic acid (**30**), 3-ethyl-4-methylthiophene-2-carboxylic acid (**31**), 3-ethyl-4,5-dimethylthiophene-2-carboxylic acid (**32**), 3-ethylthiophene-2,5-dicarboxylic acid (**33**), 3,4-dimethylthiophene-2,5-dicarboxylic acid (**34**), 4-ethyl-3-methylthiophene-2,5-dicarboxylic acid (**35**), 3,4-diethylthiophene-2,5-dicarboxylic acid (**36**), 2-acetyl-3-ethylthiophene (**37**), 2-acetyl-3-ethyl-5-methylthiophene (**38**), 2-acetyl-4-ethyl-5-methylthiophene (**39**), 2-acetyl-3-ethyl-4,5-dimethylthiophene (**40**), 2,5-diacetylthiophene (**41**), 2,5-diacetyl-3-methylthiophene (**42**), and 2,5-diacetyl-3,4-dimethylthiophene (**43**) are given in Table 3.

TABLE 3. Enthalpies of Formation of Thiophene Derivatives **22-43** in the Gas Phase, Calculated by the PM3 Method and Corrected with Equation (1)

Compound	Enthalpy of formation, kJ/mol		Compound	Enthalpy of formation, kJ/mol	
	$\Delta_f H^0_{calc}$	$\Delta_f H^{o*}_{calc}$		$\Delta_f H^o_{calc}$	$\Delta_f H^{o*}_{calc}$
22	-271.79	-297.35	**33**	-633.76	-688.45
23	-297.43	-325.05	**34**	-651.77	-707.91
24	-305.48	-333.75	**35**	-670.00	-727.61
25	-303.36	-331.46	**36**	-695.57	-755.24
26	-285.17	-311.80	**37**	-94.47	-105.75
27	-282.14	-308.53	**38**	-125.77	-139.57
28	-316.54	-345.70	**39**	-128.64	-142.67
29	-333.04	-363.53	**40**	-163.94	-180.82
30	-339.51	-370.52	**41**	-197.38	-216.95
31	-325.75	-355.65	**42**	-236.02	-258.70
32	-356.86	-389.27	**43**	-267.66	-292.88

In the present work a good correlation has therefore been established between values of the enthalpy of formation in the gas phase of certain aldehydes, ketones, and acids of the thiophene series obtained experimentally and calculated with the aid of the PM3 semiempirical quantum-chemical method. This method may therefore be recommended for thermochemical calculations on compounds of this class. A linear regression equation has been deduced describing the link between calculated and experimental values of heats of formation enabling the results of quantum-chemical calculations to be corrected maximally to approximate them to experimental values. With the aid of this method the enthalpies of formation of twenty two thiophene derivatives in the gas phase have been calculated, and may be useful when studying mechanisms of chemical reactions and in the search for means of managing them.

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