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THERMOCHEMICAL PROPERTIES OF α-NITRO DERIVATIVES OF FURAN

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The literature contains data on the thermochemical properties of furan and a few of its derivatives [furfural, 2-furyl alcohol, 1-(2-furyl)ethene, 2-furancarboxylic acid, and 3-(2-furyl)acrylic acid] [1-3].

The thermochemical properties of nitro derivatives of furan, widely used in medicine and veterinary medicine, have not been studied. In the present paper, we have measured the standard enthalpies of formation of 2-nitrofuran (Ia), 5-nitrofurfural (Ib), 5-nitro-2-furfural diacetate (Ic), methyl 5-nitro-2-furancarboxylate (Id), and 3-(5-nitro-2-furyl)acrolein (Ie) in condensed and gaseous states. The standard enthalpy was determined only in the condensed state for 5-nitrofuran-2-carboxylic acid (If), 3-(5-nitro-2-furyl)acrolein diacetate (Ig), furacilin 2-furfurylidenesemicarbazone (Ih), 5-nitro-2-furamide (Ii), and methyl 5-nitro-2-acetoxy-2,5-dihydro-2-furancarboxylate (IIb). For comparison, the thermochemical parameters were determined for furans which were not studied calorimetrically previously, namely, 2-furfural diacetate (Ij), methyl 2-furancarboxylate (Ik), and 3-(2-furyl)acrolein (II), and for the adduct of 2-furfural diacetate and acetyl nitrate 5-nitro-2-acetoxy-2,5-dihydro-2-furfural diacetate (IIa) (Tables 1 and 2).

EXPERIMENTAL

The heats of combustion ($-\Delta U_{b'}$) were determined on a setup [5] with an energy equivalent of 1277.7 ± 0.2 kcal/Ω according to [6]. During calibration of the calorimeter, a C_6H_5COOH standard was used, whose heat of combustion was 6318.1 cal/g at 25°C with weighing in vacuo. Succinic acid was used as the secondary standard substance during calibration of the calorimeter.

Tablets of the substances were weighed with a precision of ± 0.01 mg with subsequent reduction of the weight to vacuum. They were ignited with a current pulse fed from a special device via a Pt wire. A degree of combustion with respect to carbon greater than 99.94% was monitored by the generally accepted Rossini procedure. In accordance with the standard procedures, corrections were introduced for the heat of formation of HNO_3, for the heat release due to auxiliary substances, for the heat transfer between the calorimetric vessel and the shell, for the isothermality of the combustion process, etc. In the measurement of the heat of combustion, the arithmetic mean value was taken as its most probable value. The error of the measurements was calculated as the geometric mean, and the Student coefficients were taken from [7] in relation to the chosen value of the confidence probability (0.95) and the number of runs. Proceeding from the equations of the combustion reactions in oxygen, e.g.,

$$C_4H_3NO_3 + 3{,}25\ O_2 \rightarrow 4CO_2 + 1{,}5H_2O + 0{,}5\ N_2$$

and taking the heats of formation of CO_2 and H_2O to be −94.052 and −68.317 kcal/mole, we found the enthalpies of formation of the investigated substances (see Table 1).

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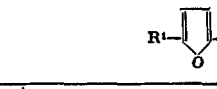
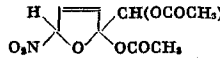
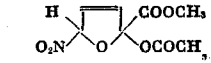
TABLE 1. Thermochemical Parameters of the Furan Derivatives in the Condensed State*

Compound				Number of runs	$-\Delta U'_b$	$-\Delta H°_c$	$-\Delta H°_f$(c)
	R^1	R^2	mp, °C				
(Ia)	NO_2	H	29	8	4025,5±0,6	453,8±0,1	24,9±0,1 (s)
(Ib)	NO_2	CHO	36	8	3687,5±0,8	518,5±0,1	54,2±0,1 (s)
(Ic)	NO_2	$CH(OCOCH_3)_2$	92	7	3871,1±1,0	939,3±0,2	214,6±0,2 (s)
(Id)	NO_2	$COOCH_3$	82	8	3648,9±0,8	622,5±0,1	112,6±0,1 (s)
(Ie)	NO_2	CH=CHCHO	118	6	4738,7±1,6	790,3±0,3	38,9±0,3 (s)
(If)	NO_2	COOH	186	8	2876,6±1,2	449,2±0,2	123,6±0,2 (s)
(Ig)	NO_2	$CH=CHCH(OCOCH_3)_2$	98	7	4471,3±1,2	1201,8±0,3	208,5±0,3 (s)
(Ih)	NO_2	$CH=N-NHCONH_2$	236–238	6	3622,2±1,4	715,8±0,3	54,0±0,3 (s)
(Ii)	NO_2	$CONH_2$	162	6	3391,6±0,6	529,7±0,1	79,4±0,1 (s)
(Ij)	H	$CH(OCOCH_3)_2$	52	7	4935,5±0,4	977,2±0,1	210,9±0,1 (s)
(Ik)	H	$COOCH_3$	bp 67°C (12 torr)	8	5251,8±0,6	661,7±0,1	107,6±0,1 (*l*)
(Il)	H	CH=CHCHO	52	7	6715,5±1,9	819,8±0,2	43,5±0,2 (s)
(IIa)			107	7	3800,6±1,3	1150,2±0,4	328,5±0,4 (s)
(IIb)			101	8	3643,0±0,9	840,1±0,2	219,7±0,2 (s)

*$\Delta U'_b$ is the heat of combustion under conditions of a calorimetric bomb, cal/g; $-\Delta H°_c$ is the enthalpy of combustion, kcal/mole; $\Delta H°_f$(c) is the standard enthalpy of formation in the condensed phase, kcal/mole (the physical state of the substance at 298°K is given in parentheses: s, solid, *l*, liquid). The solvents for crystallization were ether for compounds (Ia), (Ib), and (Il), 95% ethanol for (Ic), (Ig), (Ih), and (Ii), 30% ethanol for (Ij), methanol for (Id), benzene for (IIa), (IIb), and benzene and then 95% ethanol for (Ie).

TABLE 2. Enthalpy of Vaporization ($\Delta H°_V$) and Standard Enthalpy of Formation in the Gas Phase [$\Delta H°_{f(g)}$] of the Furan Derivatives

Compound	Determination of the enthalpy of vaporization			$-\Delta H°_f(g)$, kcal/mole
	temperature range, °C	lg P(1/T) *	$\Delta H°_V$, kcal/mole	
(Ia)	4÷25	12,75–3935,9/T	18,0±0,5	6,9±0,6
(Ib)	10÷30	9,97–4160,9/T	19,0±0,6	35,2±0,6
(Ic)	15÷45	16,60–6601,8/T	30,2±0,6	184,4±0,6
(Id)	30÷60	15,04–5448,7/T	24,9±0,5	87,7±0,5
(Ie)	45÷65	11,25–5128,6/T	23,4±0,5	15,5±0,6
(Ij)	20÷50	16,77–5734,9/T	26,2±0,6	184,7±0,6
(Ik)	–	–	10,8±0,2 †	96,8±0,5
(Il)	16÷40	10,91–3967,2/T	18,2±0,5	25,3±0,6
(IIb)	60÷90	10,35–4659,1/T	21,3±0,5	307,2±0,7

*Adopted notation: P(1/T) is the relation of the saturated vapor pressure (P, torr) to the temperature (T, °K).
†$\Delta H°_V$ for the compound (Ik) was determined by direct calorimetry according to [4]. The enthalpies of vaporization were reduced to 25°C on the basis of the approximation of Rae and Mason [4].

The enthalpies of vaporization ($\Delta H°_V$) were determined by the Knudsen effusion method [8] on the basis of measurement of the relation of the saturated vapor pressure to the temperature, for which the modified setup described in [6] was used. The experimental data were treated by the method of least squares. The obtained relations of log P (1/T) and the enthalpies of vaporization calculated from them are given in Table 2.

See [9-13] for the methods of synthesis and confirmation of the structure of the investigated furan derivatives. The samples of the compounds were purified by repeated crystallization, and the purity was monitored by thin-layer chromatography [14] and, in two cases [compounds (Ic) and (Ij), see Table 1], by a modified method of melting curves [15], for which the amount of the impurity was ≤ 0.2 mole %.

CONCLUSIONS

1. The standard enthalpies of combustion of 14 furan derivatives (including 11 α-nitro-substituted furan derivatives) were determined by a semimicro calorimetric method for the first time.

2. The standard enthalpies of vaporization of nine furan derivatives were determined by the Knudsen effusion method.

3. The standard enthalpies of formation of the investigated substances were determined in the condensed and gaseous states.

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ESTIMATION OF THE POLAR INTERACTION BETWEEN SUBSTITUTED NITROBENZENES AND A NITRILE STATIONARY PHASE AND SOME ASPECTS OF THE USE OF THE HAMMETT EQUATION

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The use of correlation equations [1, 2] in gas chromatography has significantly extended the possibilities of this method and the amount of information which it provides. For example, the logarithm of the relative retention time for alkylbenzenes and the σ constants for the substituents are related by a modified Hammett relationship, i.e., the Yukawa–Tsuno equation [3]. The gas-chromatographic behavior of a series of aliphatic compounds is described by the Hammett–Taft equation [4, 5], which takes account of the inductive and steric effects of the substituents. An additive scheme for calculating the retention indices of α,ω-substituted alkanes has also been refined with the help of this equation [6].

The activity coefficient or excess free energy [7] provides a quantitative measure of the reactivity of a sorbate–stationary phase system in the description of an equilibrium chromatographic process. In particular, it has been established that there is a linear relationship between these thermodynamic functions and the substituent constants in the case of substituted phenols, anilines [8], and aliphatic alcohols [4]. However, in the case of thermally labile compounds, such as substituted nitrobenzenes, for example, it is difficult to carry out such an analysis since the calculation of the activity coefficients and excess free energies is not accurate.

It may be postulated that when substituted nitrobenzenes are subjected to GLC on an XE-60 nitrilesilicone phase, the separation process is mainly determined by polar interactions, i.e., orientation, inductive, and specific interactions. In this case, it would be expected that there would be a correlation between the Hammett σ constants and the parameters which characterize the polar interactions between the sorbate and the stationary phase.

In the present work, a new parameter $\Delta(\delta I_{i,j})$, which is proportional to the difference in the polar contributions to the differential molar free energies of sorption for two substances and which is calculated from their retention indices, is proposed. The GLC behavior of substituted nitrobenzenes on methyl- and nitrilesilicone stationary phases and also the dependence of $\Delta(\delta I_{i,j})$ on the Hammett σ constants have been investigated.

EXPERIMENTAL

The investigations were carried out on m- and p-substituted derivatives of nitrobenzene containing the groups: CH_3, OH, NH_2, $NHCH_3$, Cl, Br, I, and NO_2 (Table 1). The reagents employed were of "pure" and "pure for analysis" grades obtained from Russian producers. 1,3,5-Trinitrobenzene and 2,4,6-trinitrotoluene were synthesized using the methods described in [9, 10] and twice recrystallized from ethanol. The temperatures at which these compounds solidified did not differ by more than 0.5°C from the values cited in the literature.

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