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BRIEF COMMUNICATIONS

Study of the Heat Capacity of the Derivatives $C_{21}H_{16}N_2O$ and $C_{21}H_{19}N_2O_2Br$ of the Alkaloid Harmine

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Abstract—Temperature dependences of the heat capacity of the alkaloid harmine derivatives 9-methoxy-2-phenyl-11*H*-indolysine[8,7-*b*]indole ($C_{21}H_{16}N_2O$) and *N*-(2)-phenacylharminium bromide $C_{21}H_{19}N_2O_2Br$ were studied by the experimental calorimetry method.

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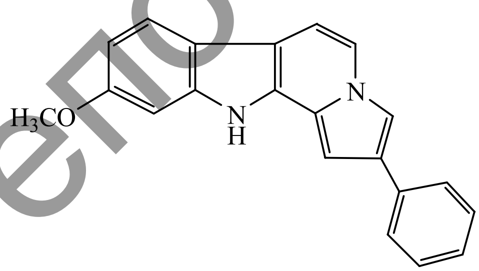
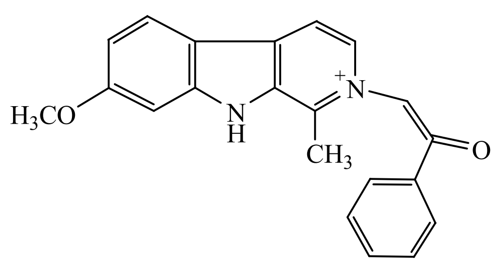
Recently the study of thermochemical properties of biologically active substances has gained a wide development in chemical thermodynamics. Such studies on the thermodynamics of natural alkaloids and their derivatives are of interest as initial data bases for fundamental data banks and for handbooks of thermochemical and thermodynamic constants. They also can be used for the directional synthesis of derivatives of analogous biologically active compounds. The majority of alkaloids represent highly active substances with a selective pharmacological action. For example, harmine and its derivatives can have cytotoxic properties [1].

The aim of this work was the experimental study of the heat capacity of harmine derivatives, 9-methoxy-2-phenyl-11*H*-indolysine[8,7-*b*]indole ($C_{21}H_{16}N_2O$) and *N*-(2)-phenacylharminium bromide $C_{21}H_{19}N_2O_2Br$ in the temperature ranges 298.15–423 and 298.15–473 K, respectively.

These compounds were synthesized for the first time in the laboratory of chemistry of alkaloids of the joint-stock company International research-and-production holding "Phytochemistry" (Karaganda) at a level of chromatographic purity and identified by physico-chemical and spectral methods of analysis [2, 3]. They have the following melting points (°C): 223–225 for $C_{21}H_{16}N_2O$ (**I**) and 280 for $C_{21}H_{19}N_2O_2Br$ (**II**). Structural formulas of the compounds are given below:



I



II

EXPERIMENTAL

The isobar heat capacity of alkaloids was studied on an IT-S-400 calorimeter. The device allows measuring temperature from –100 up to 400°C. The limiting rating measurement error is ±10.0% [4]. Graduation of the device was carried out using a copper standard. Five replicate experiments were fulfilled at each temperature in intervals of 25°, and their results were averaged. The specific heat

Experimental values of $C_{21}H_{16}N_2O$ (**I**) and $C_{21}H_{19}N_2O_2Br$ (**II**) heat capacity

T, K	$C_p\pm\bar{\delta}$, J g^{-1} K^{-1}	$C^0_p\pm\mathring{\Delta}$, J mol^{-1} K^{-1}
	Compound **I**	
298.15	0.5622±0.0132	179±12
323	0.7485±0.0197	234±17
348	1.0057±0.0293	314±25
373	1.1027±0.0250	344±22
398	1.1519±0.0314	360±27
423	1.2014±0.0297	375±26
	Compound **II**	
298.15	0.7440±0.0146	306±17
323	1.0644±0.0217	438±25
348	1.0869±0.0283	447±32
373	1.2611±0.0328	519±38
398	1.2923±0.0371	532±43
423	1.4597±0.0420	600±48
448	1.7667±0.0485	727±55
473	1.8283±0.0351	752±40

inaccuracy_ was determined by the root-mean-square deviation δ and that of mole heat capacity, by the random inaccuracy component $\mathring{\Delta}$[5].

Correctness of the experimental heat capacity values is proved by the fact that the experimental value of the standard heat capacity of sodium arsenate Na_3AsO_4 of 169.1 J mol^{-1} K^{-1} determined on the same IT-S-400 calorimeter [6] agrees satisfactorily with its recommended value of 170.3 J mol^{-1} K^{-1} given in the handbook [7]. The device operation was also checked up by the determination of α-Al_2O_3 heat capacity. The experimental value of C^0_p (298.15) 76.0 J mol^{-1} K^{-1} for α-Al_2O_3 agrees satisfactorily with its recommended value 79.0 J mol^{-1} K^{-1} [8]. The upper limit of temperature measuring (°C) was mp 100° to avoid the premelting effect.

The results of the calorimetric study are given in the table.

On the basis of the experimental data on C^0_p we have deduced equations of the type $C^0_p = a + bT + cT^{-2}$ describing the temperature dependences of the heat capacity of harmine derivatives $C_{21}H_{16}N_2O$ (**I**) and $C_{21}H_{19}N_2O_2Br$ (**II**) (J mol^{-1} K^{-1}):

$$C^0_p\,(\mathbf{I}) = (1629.23\pm 116.0) - (1940.9\pm 138.19)\times 10^3 T - (774.64\pm 55.15)\times 10^{-5} T^{-2}, \quad (1)$$

$$C^0_p\,(\mathbf{II}) = -(29.96\pm 2.04) + (1828.43\pm 124.70)\times 10^3 T - (185.50\pm 12.65)\times 10^{-5} T^{-2}. \quad (2)$$

We used values of average random errors for the whole temperature range in the equations for the temperature dependence of the heat capacity of studied substances calculated from the experimental data.

CONCLUSIONS

(1) The heat capacity of $C_{21}H_{16}N_2O$ and $C_{21}H_{19}N_2O_2Br$ was determined by the dynamic calorimetry method in the ranges 298.15–423 and 298.15–473 K. On its basis the equation of the temperature dependence of the heat capacity was deduced.

(2) The values of the standard heat capacity of 179± 12 ($C_{21}H_{16}N_2O$) and 306±17 J mol^{-1} K^{-1} ($C_{21}H_{19}N_2O_2Br$) were determined experimentally.

REFERENCES

1. Ishida, J., Wang, H.K., Bastow, K.F., et al., *Bioorg. Med. Chem. Lett*., 1993, vol. 9, no. 23, pp. 3319–3324.
2. Nurmaganbetov, Zh. S., Shults, E.E., Chernov, S.V., et al., Abstract of Papers, *2nd Annual Russian-Korean Conf. "Current Issues of Natural Products Chemistry and Biotechology,"* Novosibirsk, Russia, 2010, p. 110.
3. Nurmaganbetov, Zh.S., Shults, E.E., Chernov, S.V., et al., *Aktual'nye problemy khimii prirodnykh soedinenii* (Actual Problems of the Chemistry of Natural Compounds), Tashkent, 2009, p. 227.
4. Platunov, E.S., *Teplofizicheskie izmereniya v rezhime* (Thermal-Physics Measurements in Operating Mode), Moscow: Energiya, 1973.
5. Spiridonov, V.P. and Lopatkin, A.A., *Matematicheskaya obrabotka eksperimental'nykh dannykh* (Mathematical Treatment of Experimental Data), Moscow: Mosk. Gos. Univ., 1970.
6. Sharipova, Z.M., Kasenov, B.K., and Bukharitsyn, V.O., *Zh. Fiz. Khim*., 1991, vol. 65, no. 5, pp. 1408–1410.
7. *Termicheskie konstanty veshchestv* (Thermal Constants of Substances), Glushko, V.P., Ed., Moscow: Nauka, 1982, issue 10, part 1.
8. Robie, R.A., Hewingway, B.S., and Fisher, J.K., *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pa) Pressure at Higher Temperatures*, Washington, 1978.