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*Yu.P. Pavlovskii, S.I. Gerasimchuk, V.V. Sergeev, G.V. Melnyk, V.B. Vostres***DETERMINATION OF CRYSTALLIZATION ENTHALPIES OF SOME ORGANIC PEROXIDES BY A DIFFERENTIAL ISOTHERMAL CALORIMETER**

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We developed a method for determination of the crystallization enthalpy of organic substances in a heat-conducting calorimeter at a temperature close to 298 K. Crystallization was conducted in the MID-200 calorimeter using an ampoule technique. The volume of ampoules, which contain the supercooled liquids, was approximately 0.2 cm³. The residual pressure was 650 Pa to lessen the heat loss. A few crystals of the material under investigation were employed as the crystallization centers. Based on the results of the experiment, the crystallization enthalpies of dicumyl peroxide, peroxyoctanoic acid and di-*tert*-butylperoxy isophthalate were determined. The vaporization and sublimation enthalpies of peroxyoctanoic acid were assessed using an ampoule method in the calorimeter. It was established that dicumyl peroxide which was supercooled 14 K below the fusion temperature exhibited a 20% increase in crystallization enthalpy as compared with that calculated from the difference between vaporization and sublimation enthalpy. At the same time, the crystallization enthalpy of peroxyoctanoic acid supercooled by 5 K was equal to that calculated from the difference between vaporization and sublimation enthalpy within the limiting experimental error. The received data show that the proposed method is promising for determining the heat of crystallization of liquids that are able to exist in a supercooled state during some time.

Keywords: isothermal heat-conducting calorimeter; supercooled liquid; crystallization enthalpy; vaporization enthalpy; sublimation enthalpy; dicumyl peroxide; peroxyoctanoic acid; di-*tert*-butylperoxy isophthalate.

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Introduction

When studying the properties of substances by calorimetric method, only those calorimetry potentialities are used that are mentioned in the manuals and traditionally accepted. The heats of chemical reaction, vaporization, sublimation as well as the heats of dissolution and mixing are mostly determined by means of an isothermal heat-conducting calorimeter [1]. Expansion of the application of various types of calorimeters could allow obtaining more characteristics by using available research facilities.

The fusion (crystallization) enthalpy of materials is usually determined either by a scanning calorimeter at the melting point or by indirect methods. Indirect methods imply the calculation of a difference between sublimation and vaporization enthalpy which in turn is determined at different temperatures or by the temperature dependence of saturated vapor pressure,

the calorimetry of dissolving substances and the data of differential thermal analysis [2].

In this work, we offer the procedure for determining the crystallization enthalpy of substances using an isothermal heat-conducting calorimeter at 298 K, this technique is applied to establish the crystallization enthalpies of three different organic peroxides: dicumyl peroxide, peroxyoctanoic acid and di-*tert*-butylperoxy isophthalate.

Experimental

When determining vaporization and sublimation enthalpies of several organic peroxides in an isothermal heat-conducting microcalorimeter [3], we detected that some of them are liable to a long-term existence as supercooled liquids at room temperature. These properties of substances were used for determining crystallization enthalpies according to the method, which had been previously used for the determination of the vaporization enthalpies [4]. The

investigated substances in a liquid state were placed in thin-walled glass spherical ampoules ($\sim 0.2 \text{ cm}^3$) with a tapered tip and sealed. Afterwards, the ampoule was carried into a glass cell of the calorimeter; the trace crystals of the material under investigation were put onto the bottom of the cell as crystallization centers. The calorimeter temperature was kept slightly below the melting temperature, but sufficient for the investigated material to be in a supercooled liquid state for some time. To avoid heat loss to air from the open-ended cell, the absolute pressure was set to about 650 Pa, which is higher than the saturation vapor pressure of the investigated compounds at experimental temperature [5].

Starting from the breaking of the ampoule in the calorimeter, the calorimetric signal was recorded, which was caused by the heat release during material's crystallization. After finishing the experiment, the specific crystallization enthalpy (J g^{-1}) was calculated according to the following equation:

$$\Delta_{\text{cryst}}H = K \cdot \Sigma / m,$$

where $K = 7.130 \pm 0.016$ is the constant of the calorimetric cell (W V^{-1}); m is the crystallizing material weight (g); Σ represents the digital integrator reading (V s).

The constant of the calorimetric cell was the same as when measuring vaporization enthalpies at 298 K and it was determined in much the same way by vaporizing substances with the reliable vaporization values ($\Delta_{\text{vap}}H_{298}$) of decane, dodecane and tetradecane that are accepted to be 51.42 ± 0.21 , 61.52 ± 0.62 and $71.73 \pm 0.72 \text{ kJ mol}^{-1}$, respectively [6]. In our opinion, this was completely enough since the crystallization experiments were carried out practically in identical conditions and in a slightly rarefied medium. To eliminate the systematic error in some isolated experiments, we determined the calorific effect of ampoule breaking, which was less than 0.01 J and less than the calorimeter sensitivity within the investigated experimental range of crystallization enthalpy.

The crystallization enthalpies of dicumyl peroxide ($\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2\text{-OO-C}(\text{CH}_3)_2\text{-C}_6\text{H}_5$), di-*tert*-butylperoxy isophthalate ($((\text{CH}_3)_3\text{C-OO-CO-C}_6\text{H}_4\text{-CO-OO-C}(\text{CH}_3)_3)$) and peroxyoctanoic acid ($\text{CH}_3(\text{CH}_2)_6\text{CO-OOH}$) were determined according to the proposed method. Among these substances, di-*tert*-butyl peroxy terephthalate also had the property of being in a supercooled state for a long time. However, its crystallization, even in the presence of the crystals, lasted several days, which did not allow measuring its crystallization enthalpy.

Technical dicumyl peroxide was purified via threefold crystallization from methanol and subsequent chromatography through aluminium oxide.

Peroxyoctanoic acid was synthesized by the reaction of octanoic acid, hydrogen peroxide and sulfuric acid which were taken in a 1:1:1 molar ratio, respectively. 60% solution of H_2O_2 was dropwise added to the solution of octanoic acid in 96% H_2SO_4 initially cooled to 273 K, the temperature being kept no more than 290 K. After completion of the reaction, the mixture was poured out onto crushed ice and the peroxyacid sediment was filtered off. The peroxyoctanoic acid was purified by double crystallization from hexane and subsequent sublimation *in vacuo* at 13.3 Pa and 301 K.

Di-*tert*-butylperoxy isophthalate was synthesized by the reaction of sodium salt of *tert*-butyl hydroperoxide with isophthaloyl dichloride at 273–278 K. The product was purified via threefold crystallization from a diethyl ether-hexane mixture (1:1 (vol.)).

The synthesized peroxides were identified by elemental analysis, iodometric determination of active oxygen and IR spectrometry. A fusion curve method [7] was used to estimate the purity of the investigated substances.

Tables 1–3 shows the primary experimental data regarding the crystallization enthalpies of the investigated substances except peroxyoctanoic acid, the vaporization and sublimation enthalpies of which were found by an ampoule method [4].

Table 1
Primary data regarding experimental determination of the crystallization enthalpies of the peroxides under investigation

T, K	$m \cdot 10^3, \text{ g}$	$\Sigma, \text{ V s}$	$-\Delta_{\text{cryst}}H, \text{ J g}^{-1}$
Dicumyl peroxide, s-l			
298.2	123.69	1.5097	87.03
297.9	129.21	1.5783	87.09
297.9	140.21	1.7077	86.84
298.0	172.21	2.1010	86.99
di- <i>tert</i> -Butylperoxy isophthalate, l-g			
298.3	141.55	1.4053	70.79
298.3	155.03	1.5428	70.96
298.0	134.20	1.3727	72.93
298.0	117.40	1.2008	72.93
298.4	178.53	1.7992	71.86
Octaneperoxoic acid, l-g			
300.2	74.67	2.0235	193.2
300.2	73.69	1.9788	191.5
299.9	81.38	2.1707	190.2
299.8	101.06	2.7682	195.3
299.9	113.79	3.1550	197.7

Table 2
Primary data regarding the experimental determination of the sublimation enthalpy of octaneperoxoic acid

T, K	m·10 ³ , g	Σ, V s	Δ _{sub} H, J g ⁻¹
298.2	34.42	2.8623	592.9
298.3	39.94	3.2794	585.4
298.4	56.06	4.6179	587.3
298.4	42.97	3.5118	582.7
298.3	35.91	2.9293	581.6
298.3	39.29	3.2406	588.1
			Average 586.3

Table 3
Primary data regarding the experimental determination of the vaporization enthalpy of octaneperoxoic acid

T, K	m·10 ³ , g	Σ, V·s	Δ _{vap} H, J/g ⁻¹
308.1	45.17	2.4933	393.6
308.2	45.48	2.4821	389.1
308.1	61.30	3.3291	387.2
308.3	67.74	3.5240	370.9
308.4	61.17	3.3132	386.2
308.2	45.72	2.4855	387.6
			Average 385.8

vaporization and sublimation enthalpies taken from [3] is closer to the value given elsewhere [8], where the fusion enthalpy was determined in an adiabatic calorimeter at fusion temperature ($\Delta_{\text{fus}}H_{312.4} = 28.14 \text{ kJ mol}^{-1}$). The observed 20% difference cannot be explained by the fact that the crystallization temperature of supercooled dicumyl peroxide is 14 K lower than the fusion temperature, since the calculation [2,6] gave only a 5% decrease in the fusion enthalpy. It is quite possible that this difference is caused by the formation of primary structures within the supercooled liquid and correspondingly gives a significant reduction in the crystallization caloric effect.

Standard deviations of the average values of thermodynamic characteristics given in Table 4 were calculated using Student's test for the confidence level of 0.05.

We realize that the developed method cannot be widely used; it is applicable only to the substances that are disposed to be in a supercooled state for a long period of time. However, in our opinion, this is not a very rare case for rather pure substances.

Table 4
Phase transition enthalpies for investigated substances

Substance	T _{fus} , K	Substance purity, mol. %	Phase transition (T, K)	Δ _{trans} H, kJ mol ⁻¹
Dicumyl peroxide	312.0±0.2	99.93	supercooled liquid–solid (298.0)	-23.52±0.17
			solid–gas (308.4) [3]	108.0±2.9 [3]
			liquid–gas (313.0) [3]	80.78±0.78 [3]
			liquid–solid	-27.42±3.0*
Di- <i>tert</i> -butylperoxy isophthalate	328.8±0.2	99.91	supercooled liquid–solid (298.2)	-22.31±0.51
Octaneperoxoic acid	305.0±0.2	99.60	supercooled liquid–solid (300.0)	-31.01±0.75
			solid–gas (298.3)	96.4±1.2
			liquid–gas (308.2)	64.4±1.6
			liquid–solid	-32.0±2.0*

* Note: Calculated by the subtraction of the vaporization and sublimation enthalpies.

Results and conclusions

Based on the experimental calorimetric measurements, the molar enthalpies for the phase transition of the investigated compounds were calculated (Table 4). It can be seen that the crystallization enthalpy of peroxyoctanoic acid, which was calculated as the sublimation enthalpy subtracted from the vaporization one, is equal to that determined by the calorimetric method within an error limit. Meanwhile, the crystallization enthalpy of dicumyl peroxide which is calculated by subtraction the

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ВИЗНАЧЕННЯ ЕНТАЛЬПІЙ КРИСТАЛІЗАЦІЇ ДЕЯКИХ ОРГАНІЧНИХ ПЕРОКСИДІВ В ДИФЕРЕНЦІЙНОМУ ІЗОТЕРМІЧНОМУ КАЛОРИМЕТРІ

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Запропоновано методику визначення ентальпії кристалізації органічних речовин в ізоترمичному теплопровідному калориметрі за температури, що близька до 298 К. Процес кристалізації здійснювали на калориметрі MID-200 із застосуванням ампульної методики. Об'єм ампул, що містили переохолоджені рідини, складав близько 0,2 см³, залишковий тиск для зменшення тепловтрат 650 Па. Для ініціювання процесу кристалізації використовували деяку невелику кількість кристалів речовини, що досліджувалась, як центри кристалізації. Наведено результати визначення ентальпій кристалізації дикумилпероксида, пероксиоктанової кислоти і ди-*трет*-бутилпероксиізопталату. Також калориметрично за ампульною методикою визначені ентальпії випаровування і сублимації пероксиоктанової кислоти. Встановлено, що ентальпія кристалізації переохолодженого на 14 К нижче температури плавлення дикумилпероксида на 20% більша, за розраховану за різницею ентальпій випаровування і сублимації. У той же час, ентальпія кристалізації переохолодженої на 5 К пероксиоктанової кислоти, в межах похибки експерименту, збігається з розрахованою за різницею ентальпій випаровування і сублимації. Одержані експериментальні дані демонструють можливість використання даної методики для визначення теплоти кристалізації рідин, які здатні певний час знаходитися в переохоложеному стані.

Ключові слова: ізоترمичний теплопровідний калориметр, переохолоджена рідина, ентальпія кристалізації, ентальпія випаровування, ентальпія сублимації, дикумилпероксид, пероксиоктанова кислота, ди-*трет*-бутилпероксиізопталат.

DETERMINATION OF CRYSTALLIZATION ENTHALPIES OF SOME ORGANIC PEROXIDES BY A DIFFERENTIAL ISOTHERMAL CALORIMETER

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We developed a method for determination of the crystallization enthalpy of organic substances in a heat-conducting calorimeter at a temperature close to 298 K. Crystallization was conducted in the MID-200 calorimeter using an ampoule technique. The volume of ampoules, which contain the supercooled liquids, was approximately 0.2 cm³. The residual pressure was 650 Pa to lessen the heat loss. A few crystals of the material under investigation were employed as the crystallization centers. Based on the results of the experiment, the crystallization enthalpies of dicumyl peroxide, peroxyoctanoic acid and di-*tert*-butylperoxy isophthalate were determined. The vaporization and sublimation enthalpies of peroxyoctanoic acid were assessed using an ampoule method in the calorimeter. It was established that dicumyl peroxide which was supercooled 14 K below the fusion temperature exhibited a 20% increase in crystallization enthalpy as compared with that calculated from the difference between vaporization and sublimation enthalpy. At the same time, the crystallization enthalpy of peroxyoctanoic acid supercooled by 5 K was equal to that calculated from the difference between vaporization and sublimation enthalpy within the limiting experimental error. The received data show that the proposed method is promising for determining the heat of crystallization of liquids that are able to exist in a supercooled state during some time.

Keywords: isothermal heat-conducting calorimeter; supercooled liquid; crystallization enthalpy; vaporization enthalpy; sublimation enthalpy; dicumyl peroxide; peroxyoctanoic acid; di-*tert*-butylperoxy isophthalate.

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