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Study of Thermochemical Properties of Diphenyl[dialkyl(alkyl)carbamoylmethyl]phosphine Oxides

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Abstract—The synthesis and the studies of properties of diphenyl[dialkyl(alkyl)carbamoylmethyl]phosphine oxides by differential scanning calorimetry, mass spectrometry and Knudsen effusion method were performed. The thermodynamic parameters of melting and vaporization were calculated.

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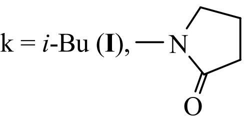
Currently, the development of materials for organic light-emitting diodes (OLED) is an important task for molecular electronics and applied synthetic chemistry. The lanthanide complexes with organic ligands, in our view, are most suitable for such application, since they possess electroluminescent properties, as has been shown previously [1].

The luminescence intensity of lanthanide ions increases sharply at the formation of complexes with organic ligands of a specific type [2]. To date, among the derivatives of rare earth metals the best results at the use as electroluminescent materials in OLED-devices showed β-diketonate, carboxylate, pyrazolonate, and hydroxyquinolinate complexes. The search for new organic ligands for lanthanide complexes for constructing OLED-devices has been limited by the use of oxygen- and nitrogen-containing compounds. However, more recently was found that high electroluminescent activity posess the complex of terbium with phosphorus-containing imidodiphosphinate ligands $Tb[Ph_2P(O)NP(O)Ph_2]_3$ [3]. As another type of promising phosphorus ligands can act diphenyl [dialkyl(alkyl)carbamoylmethyl]phosphine oxides of general formula $Ph_2P(O)CH_2C(O)NR^1R^2$. For the targeted synthesis of new rare-earth metal complexes with ligands of this type are needed the data on the thermal behavior of the parent ligands, such as enthalpy and entropy of melting and vaporization, and the composition of the vapor phase, fragmentation of the compounds under electron impact, etc.

We synthesized compounds **I** and **III** by amidation of ethyl diphenylphosphorylacetic acid in alcohol solution at room temperature.

$$Ph_2P(O)CH_2C(O)OEt + H_2NAlk \rightarrow Ph_2P(O)CH_2C(O)NHAlk,$$

I, III

Alk = *i*-Bu (**I**),  (**III**).

Synthesis of compound $Ph_2P(O)CH_2C(O)N(Bu)_2$ (**II**) was carried out using Arbuzov reaction of ethyl esters of trivalent phosphorus with chloroacetamide:

$$Ph_2P(OEt) + ClCH_2C(O)N(Bu)_2 \rightarrow Ph_2P(O)CH_2C(O)N(Bu)_2.$$

II

The compounds **I**–**III** were obtained in 70–90% yield. They are stable in air, light colored fine-

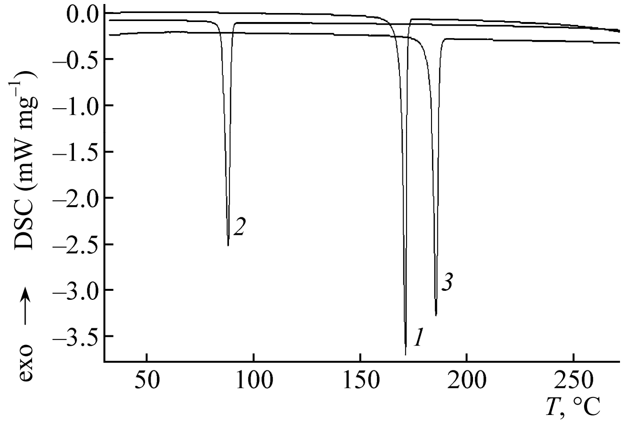


Fig. 1. DSC curves of the compounds **I–III.**

crystalline materials. Their structure was confirmed by elemental analysis, IR and NMR spectroscopy. The solubility of compounds in organic solvents are quite different [4, 5].

Differential scanning calorimetry. The study of phase transitions of the samples **I–III** in the range of 30–300°C was performed using a differential scanning calorimeter DSC204F1 of Netzsch Geratebau, Germany. The design of the calorimeter DSC204F1 and working procedure are similar to the described in [6]. Checking the reliability of the calorimeter was performed using standard calibration experiments to measure the thermodynamic characteristics of melting of *n*-heptane, mercury, indium, tin, lead, bismuth and zinc. As a result, it was found that the apparatus and the measurement technique provide ability of measuring the temperature of physical transformations with an accuracy ±0.2 K, the enthalpies of transitions ±1%. Calorimetric measurements for the complexes were carried out in an argon atmosphere at a heating rate of 5 K min^{-1}. Within the sensitivity of the method the studied substance is an individual phase. In this temperature range the samples underwent only one phase transformation, the melting. From the data of differential scanning calorimetry (DSC) of compounds **I–III** were found the melting temperatures of the complexes and the fusion thermodynamic parameters (Fig. 1, Table 1).

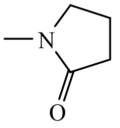
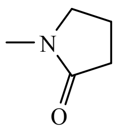
Table 1. Standard thermodynamic parameters of the melting process of compounds **I–III**

Comp. no.	mp, °C	$\Delta H_{\text{melting}}$, kJ mol^{-1}	$\Delta S_{\text{melting}}$, J mol^{-1} K^{-1}
I	165	29.7	67.9
II	80	30.2	85.7
III	174	41.7	93.3

Mass-spectrometric investigation. Analysis of the mass spectra showed that the composition of the vapor molecules corresponds to the chemical formula $Ph_2P(O)CH_2C(O)NR^1R^2$. At the ionization by electrons the compounds **I–III** exert similar fragmentation. The main peaks and relative intensities of ions in the mass spectra are shown in Table 2.

Vapor pressure. The temperature dependence of the vapor pressure of the complexes (Fig. 2) was measured by the Knudsen effusion method with the registration of sublimed substance by weight in the temperature range 100–216°C. The dependence is expressed by the equation: $\log [p\ (\text{mm Hg})] = AB/T$. The coefficients are listed in Table 3. From the *P–T* plot were calculated the thermodynamic parameters of sublimation and evaporation (Table 4). The tempera-

Table 2. Major peaks and relative ion intensities in the mass spectra of compounds **I–III**

Ion	I_{rel}, %
$Ph_2P(O)CH_2C(O)NHBu^i$	
$[Ph_2P(O)]^+$	88
$[Ph_2P(O)CH_2]^+$	65
$[Ph_2P(O)CH_2C(O)]^+$	92
$[Ph_2P(O)CH_2C(O)NH]^+$	100
$[Ph_2P(O)CH_2C(O)NHC]^+$	51
$Ph_2P(O)CH_2C(O)NHBu^i$	93
$Ph_2P(O)CH_2C(O)NBu_2$	
$[Ph_2P(O)]^+$	64
$[Ph_2P(O)CH_2]^+$	100
$[Ph_2P(O)CH_2C(O)]^+$	79
$Ph_2P(O)CH_2C(O)NBu_2$	39
$Ph_2P(O)CH_2C(O)NH(CH_2)_3$ 	
$[Ph_2P(O)]^+$	52
$[Ph_2P(O)CH_2]^+$	91
$[Ph_2P(O)CH_2C(O)]^+$	87
$[Ph_2P(O)CH_2C(O)NHCH_2]^+$	100
$[Ph_2P(O)CH_2C(O)NH(CH_2)_2]^+$	71
$Ph_2P(O)CH_2C(O)NH(CH_2)_3$ 	41

ture range of vaporization was chosen according to the DSC data. In the studied temperature range no processes except vaporization observed. In addition, according to the data of mass spectrometry, at the heating does not occur association of molecules, so the calculation of the vapor pressure of sublimation and evaporation was carried out assuming formation of monomeric vapor.

EXPERIMENTAL

N-Isobutylcarbamoylmethyldiphenylphosphine oxide (**I**) [4] and *N,N*-dibutylcarbamoylmethyldiphenylphosphine oxide (**II**) [5] were prepared by the described methods. Their physical and chemical constants coincide with published data.

2-(Diphenylphosphoryl)-*N*-[3-(2-oxopyrrolidin-1-yl)propyl]acetamide (III) was prepared as described in [4] by direct amidation of ethyl diphenylphosphorylacetic acid with 1-(3-aminopropyl)pyrrolidin-2-one in EtOH. Yield 75%. ^{31}P NMR spectrum (121.5 MHz, $CDCl_3$), δ_P, ppm: 29.7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.58 quintet (2H, $(O)CNHCH_2C\underline{H}_2$, $^3J_{HH}$ = 6.9); 1.97 quintet (2H, $C(O)CH_2C\underline{H}_2$, $^3J_{HH}$ = 7.7); 2.34 quintet (2H, $C(O)CH_2$, $^3J_{HH}$ = 7.7); 3.16 t (2H, NCH_2, $^3J_{HH}$ = 6.8), 3.17 t (2H, NCH_2, $^3J_{HH}$ = 6.8), 3.26 t (2H, NCH_2, $^3J_{HH}$ = 7.1), 3.30 d (2H, PCH_2, $^2J_{PH}$ = 12.9), 7.42–7.50 m (5H, CH_{Ar} + NH), 7.50–7.56 m (2H, CH_{Ar}), 7.70–7.78 m (4H, CH_{Ar}). IR spectrum (KBr, ν, cm^{-1}): 510, 527, 730, 1120, 1176 (P=O), 1289, 1317, 1435 (CH_2 def), 1544, 1666 (C=O), 2910, 2943, 2965 , 3060, 3277. Found, %: C 65.41, H 6.58, N 7.38. $C_{21}H_{25}N_2O_3P$. Calculated, %: C 65.61, H 6.56, N 7.29.

Mass-spectrometry. The mass spectra of compounds were registered on a Polaris Q/Trace GC Ultra gas chromatography-mass spectrometer. The temperature of the ion source 250°C, the range of the measured masses 50–990, electron energy 70 eV, heating rate 100°C per minute.

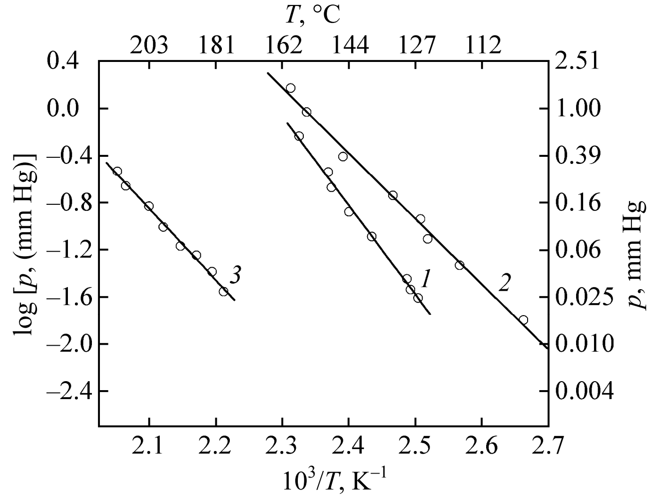


Fig. 2. Plots of the saturated vapor pressure of the complexes **I–III** log [*p*, (mm Hg)] = *f* (10^3/*T*): (*1*) **I**, (*2*) **II**, (*3*) **III**.

Vapor pressure. The vapor pressure of compounds was measured by the Knudsen effusion method with the registration of weight of the sublimed substance. The vapor pressure values were calculated using the Hertz–Knudsen equation:

$$p = 17.14\frac{\Delta m}{\sigma_{\mathrm{eff}}\tau}\sqrt{\frac{T}{M}},$$

where *p* is the measured vapor pressure, mm Hg; Δ*m* is the amount of evaporated substance, g; σ_{eff} is the area of the effusion hole, cm^2 ($\sigma_{\mathrm{eff}} = 1.46\times10^{-3}$ cm^2); τ is the evaporation duration, s, *T* is the evaporation temperature, K, and *M* is molecular weight of the vapor. Sensitivity of the McBain balances was 1.0156 g per 1 cm of the cathetometer KM-8 scale.

Table 3. Coefficients of the equation: log [*p*, (mm Hg)] = *A*–*B*/*T*, for compounds **I–III**

Comp. no.	A	*B*, 10^{-3}	R^2 ^{a}
I	17.32±0.56	7.56±0.23	0.997
II	12.97±0.44	5.56±0.18	0.997
III	11.88±0.45	6.06±0.21	0.996

[a] R^2 is the confidence factor of the approximation.

Table 4. Thermodynamic parameters of the process of vaporization of the complexes **I–III**

Comp. no.	Process	Δ*T*, °C	ΔH_{tr} (*T**),^{a} kJ mol^{-1}	ΔS_{tr} (*T**),^{a} J mol^{-1} K^{-1}
I	Sublimation	126–160	144.8±4.4	276.5±10.7
II	Vaporization	102–160	106.5±3.4	193.2±8.4
III	Vaporization	170–214	116.0±4.0	172.3±8.6

[a] *T** is the middle point of the studied temperature range.

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