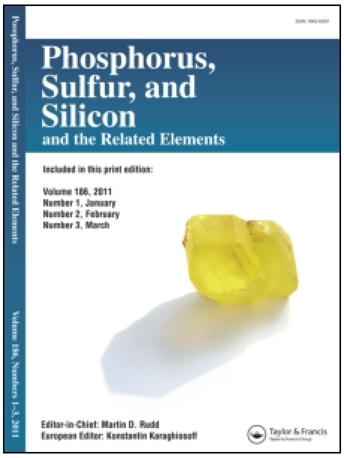

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Thermochemistry of Heteroatomic Compounds XXI: Heat Capacities of Some Derivatives of Methylphosphonic and Dithiophosphorus Acids*

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The heat capacities of 2,4-dimethyl-2-oxo-(I)-, 2,5,5-trimethyl-2-oxo(II)-1,3,2-dioxaphosphorinanes, methylphosphonic acid (III), O,O-dimethyl(IV)-, O,O-diethyl(V)-, O,O-di-isopropyl(VI)esters of dithiophosphorus acid, 4,5-dimethyl-2-thiono-2-mercapto-1,3,2-dioxaphospholane(VII), and 4-methyl-2-thiono-2-mercapto-1,3,2-dioxaphosphorinane(VIII) were determined using the scanning calorimetry.

Keywords Heat capacity; methylphosphonic acid; dithiophosphorus esters

INTRODUCTION

The problem of the chemical characteristic determination of the tetracoordinated phosphorus derivatives could be solved in many cases with the use of the reaction calorimetry.[2] As a rule, that are the hydrolysis, ester-formation and other akin processes, which often could be carried out in conditions distinct from the standard requirements. In particular, the hydrolysis processes of cyclic and acyclic esters of methylphosphonic and dithiophosphorus acids carry out in the full volumes (98–99%) at 333–353 K [Eqs. (1) and (2)]:

$$\underset{\text{I, II}}{\mathrm{MeP(O)O_2R}} + 2\mathrm{H_2O} \rightarrow \underset{\text{III}}{\mathrm{MeP(O)(OH)_2}} + \mathrm{HOROH} \qquad (1)$$

$$(\mathrm{I}): \mathrm{R} = -(\mathrm{CH_2})_2\mathrm{CH(Me)}-, (\mathrm{II}): \mathrm{R} = -\mathrm{CH_2C(Me)_2CH_2} - (\mathrm{II});$$

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*Part XX, see Ref.[1]

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$$(RO)_2P(S)SH + 4H_2O \rightarrow H_3PO_4 + 2ROH\,(\text{or}\,HOROH) + 2H_2S, \quad (2)$$

IV–VIII

$$(IV): R = Me, (V): R = Et, (VI): R = i-Pr, (VII):$$

$$R = -CH(Me)CH(Me)-,$$

$$(VIII): R = -(CH_2)_2CH(Me)-.$$

EXPERIMENTAL

The heat capacities of all compounds were measured at 310–370 K in a "Setaram"-calorimeter DSC-111 in the conditions of the line increase of temperature (3° min^{-1}). The calibration of calorimeter has been carried out taking into account the dependence of the corundum heat capacity from temperature.[4] The error in the determination of C_p values consists of no more then ±4–5%.

All substances (I–VIII) were synthesized by previously reported methods[5,6] and have physical constants in accordance with the literature values. The purity of the compounds has been controlled with the use of element analysis and IR and NMR spectra and consisted of no less then 98–99%.

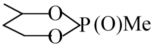
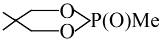
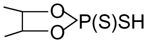
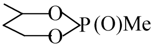
RESULTS AND DISCUSSION

Taking into account these circumstances, we believe that the determination of the heat capacities of the all compounds of Eqs. (1) and (2) is necessary for the recalculation of thermochemical parameters from the high temperature, on which they have been produced, into the temperature 298.15 K.

In the connection of the above-mentioned facts, the isobaric heat capacities (C_p) of compounds (I–VIII) have been determined in the temperature range 310–370 K (Table I). Moreover, we also determined the heat capacities of diatomic alcohols [$HO(CH_2)_2CH(Me)OH$ (IX), $HOCH(Me)CH(Me)OH$ (X)] because they are formed among the products of reaction (1) and (2). It is necessary to note that the C_p-magnitude of compound (IX, Table I) corresponds to 1,4-butanediol (200.1 J mol^{-1} K^{-1}) value, which represented in the review.[3] We must also remark that the heat capacity values of (I–III, XI, X) are in the straight dependence from the temperature [Eq. (3)]; the parameters of this equation are summed in Table I.

$$C_p = a + bT. \quad (3)$$

TABLE I The parameters of Eq. (3.*r*.) is the Correlation Coefficient, and S_0 is Standard Deviation) and the Calculated C_p-Values (J mol^{-1} K^{-1}) for Compounds(I–X).

No	Compound	*a*	*b*	*R*	S_0	C_p
I		138.0	0.34	0.987	1.17	239.4 ± 12.0
II		−55.0	0.88	0.999	0.98	207.4 ± 8.3
III	$MeP(O)(OH)_2$	35.0	0.25	0.996	0.47	109.5 ± 5.5
IV	$(MeO)_2P(S)SH$	—	—	—	—	219.0 ± 8.5
V	$(EtO)_2P(S)SH$	—	—	—	—	267.1 ± 5.9
VI	$(iPrO)_2P(S)SH$	—	—	—	—	343.0 ± 5.1
VII		—	—	—	—	251.2 ± 7.9
VIII		—	—	—	—	285.9 ± 4.7
IX	$HO(CH_2)_2CH(Me)OH$	−146.0	1.18	0.983	5.22	205.8 ± 10.3
X	HOCH(Me)CH(Me)OH	42.0	0.64	0.982	2.88	232.8 ± 11.6

Another picture we observed was for the esters of dithiophosphorus acid (IV–VIII). The temperature did not affect the heat capacities of these compounds. Due to this, the average values of their C_p have been calculated in the interval of 310–370 K. Probably the exchange of oxygen atoms at phosphorus on the sulfur responds for the abovementioned phenomena. However, it is necessary to note that the heat capacity values for acyclic dithiophosphoric derivatives (IV–VI) show the obvious distinctions due to the space structure of alkoxy-radicals at a phosphorus atom.

CONCLUSION

The heat capacity values have been determined for the phosphonic and dithiophosphorus acids of the acyclic and cyclic space structure in the range of 310–379 K. The C_p-values depends in these conditions from the temperature for the phosphonic derivatives only; the heat capacities magnitudes of dithiophosphorus acid esters are not subjected to this influence that probably could be explained by the exchange of two oxygen atoms on sulfur at phosphorus.

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