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Thermochemical and theoretical study of 2-oxazolidinone and 3-acetyl-2-oxazolidinone

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ABSTRACT

In this paper, standard molar energies of combustion of 2-oxazolidinone and 3-acetyl-2-oxazolidinone are reported. The experimental values, obtained from static-bomb combustion calorimetry, are $-(1465.42 \pm 0.52)$ kJ·mol^{-1} and $-(2350.86 \pm 0.84)$ kJ·mol^{-1}, respectively.

Using these combustion energy values, the standard molar enthalpies of formation, in crystalline phase, for the aforesaid compounds were calculated. These values were also determined, and the corresponding values are $-(430.30 \pm 0.96)$ kJ·mol^{-1} and $-(617.72 \pm 1.58)$ kJ·mol^{-1}, respectively.

The standard molar enthalpies of sublimation at $T = 298.15$ K were experimentally obtained by using the well-known Knudsen effusion method. The obtained values are (84.20 ± 3.22) kJ·mol^{-1} and (82.36 ± 1.84) kJ·mol^{-1}, respectively.

From the above experimental results, the standard molar enthalpies of formation in gas-phase of the compounds were derived. The values are: $-(346.10 \pm 3.36)$ kJ·mol^{-1} and $-(535.36 \pm 2.43)$ kJ·mol^{-1}, respectively.

To support the consistency of the experimental results presented here, enthalpies of formation in gas-phase, using the G4 composite method, were carried out as well.

Experimental results suggest that the formation of intermolecular hydrogen bonds between the nitrogen (at ring's position 3, see Fig. 1) with the oxygen (at ring's position 2, see Fig. 1) contributes to the values of temperature and enthalpy of fusion, enthalpy of sublimation, and enthalpy of formation in solid phase.

1. Introduction

Oxazolidinones conform a class of cyclic urethanes, which have many and varied important applications in the field of chemistry. In organic chemistry, for instance, they are used as chiral auxiliary for the asymmetric synthesis [1]. Due to their versatile properties, oxazolidinones are frequently used in the synthesis of important drugs, such as antibiotics [1–3], and other significant organic molecules [5], and also as polymer precursors [4]. In particular, derivatives of 2-oxazolidinone substituted at the 3-position are useful as synthetic reagents, additives, and inhibitors of protein synthesis in gram-positive bacteria, which shows significant antibacterial and fungicidal activity [6].

Because of the biological and pharmaceutical importance of these substances, it is interesting to make thermochemical studies in order to establish a relationship between their molecular structure and their possessed energy, from the experimental determination of their thermodynamic properties. Knowledge of these properties is necessary because it allows the understanding of the behavior of these substances and their relative stabilities.

In this work, thermochemical properties of 2-oxazolidinone (hereafter 2O) and 3-acetyl-2-oxazolidinone (hereon 3A2O), whose structures are shown in Fig. 1, were obtained. The standard molar enthalpy of formation in solid phase, $\Delta_f H^\circ_m$ (cr, 298.15 K), of both compounds were obtained from the standard molar energy combustion values, which in turn were determined through static-bomb combustion calorimetry. The enthalpies of sublimation, $\Delta^g_{cr} H^\circ_m$, at $T = 298.15$ K, were derived indirectly by measuring the vapor pressure of these compounds, using the Knudsen effusion method. From the experimental results, the standard molar enthalpies of formation in gas-phase, $\Delta_f H^\circ_m$ (g, 298.15 K), were calculated.

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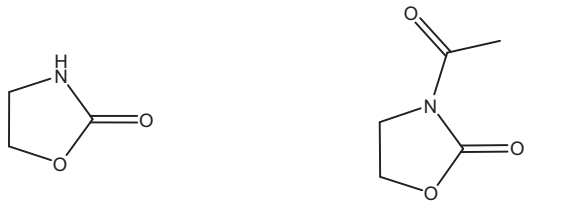

2-oxazolidinone (2O) 3-acetyl-2-oxazolidinone (3A2O)

Fig. 1. The molecular structure of 2-oxazolidinone (2O) and 3-acetyl-2-oxazolidinone (3A2O).

2. Experimental procedure

2.1. Materials

The compounds 2-oxazolidinone (CAS number: 497-25-6) and 3-acetyl-2-oxazolidinone (CAS number: 1432-43-5) were commercial products, supplied by Aldrich Co., whose purities are marked as >98% and >99% respectively. 2O was purified by repeated recrystallization from a 2:1 mixture of ethyl acetate and acetone (HPLC grade). This procedure substantially improved the purity of the compound. 3A2O was used without additional purification. Table 1 summarizes the chemical data, sources and purities of the substances studied and the calorimetric standards used in this work. In order to avoid the presence of water in the samples, they were placed in an oven at $t = 50$ °C for 48 h before conducting the combustion experiments.

2.2. Differential scanning calorimetry

Purities (x), melting temperatures (T_{fus}) and melting enthalpies ($\Delta^{l}_{cr}H^{\circ}_{m}$) of the compounds were determined, using a 2010 TA Instruments differential scanning calorimeter, by the technique fractional melt [7].

All experiments were performed with an unsealed aluminium cell, which were subjected to a constant nitrogen flow of 60 $cm^3 \cdot min^{-1}$. The masses of the samples used in the DSC experiments were between 2 and 5 mg, and they were measured with a Mettler Toledo UMX2 electronic microbalance, which has a 0.1 μg accuracy. Purities, given in mole fraction, were determined by DSC, and the measured values were $x = (0.9997 \pm 0.0002)$ and $x = (0.9970 \pm 0.0009)$ for 2O and 3A2O, respectively.

To determine the compounds' purity, calibration in energy and temperature of the calorimeter was carried out using the fusion of high-purity indium [7].

The heat capacity (C_p) of the compounds was determined by applying the comparison method [8,9], using synthetic sapphire as a reference material, in the temperature range from 273.15 K to 333.15 K.

Table 2 shows the physical properties of all substances used in the combustion experiments and the results obtained by DSC. The uncertainties correspond to twice the standard deviation of the mean.

2.3. Combustion calorimetry

The combustion energy of the compounds was determined with a static-bomb isoperibolic calorimeter. This device has an 1108 stainless steel Parr combustion bomb, which has an internal volume of 0.345 dm^3, wherein the combustion reaction takes place.

The calibration of this equipment was validated in a previous work [14], and the calibration method consisted on reproducing the thermodynamic properties of standard benzoic acid (Reference Standard Material 39j) certified by NIST, which has an energy of combustion well known as $\Delta_c u = -(26{,}434 \pm 3)\ J \cdot g^{-1}$ under certified conditions [15]. The value of calorimetric equivalent is ε (calor) = $(10150.8 \pm 1.2)\ J \cdot K^{-1}$, where the uncertainty is the standard deviation of the mean. The experiments of calibration and combustion of the compounds were performed under similar conditions, as explained below.

One cm^3 of deionized water was placed into the bomb along with the platinum crucible containing the sample in pellet form. The bomb was purged for 5 min in order to remove any air traces, and then it was filled with high purity oxygen (Airgas Corp., $x = 0.99999$) at a pressure of 3.04 MPa.

The masses of the substances used in the combustion were measured with a Sartorius ME 215S balance, which has a 0.01 mg accuracy.

Table 1
Chemical data, sources and purities of the substances utilized in this work.

Chemical name	CAS number	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
2-Oxazolidinone	497-25-6	Aldrich	>0.98	Recrystallization	0.9997 ± 0.0002	DSC
3-Acetyl-2-oxazolidinone	1432-43-5	Aldrich	>0.99	None	0.9970 ± 0.0009	DSC
Indium	7440-74-6	NIST	0.999999			
Aluminium oxide	1344-28-1	NIST	0.9995			

Table 2
Physical properties of the compounds under study and of all the materials which took part in the combustion processes at $P^{\circ} = 0.1$ MPa.

Compound	$\frac{M}{g \cdot mol^{-1}}$	$\frac{-(\partial u/\partial p)_T}{J \cdot g^{-1} \cdot MPa^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{x}{mol\ fraction}$	$\frac{\Delta^{l}_{cr}H^{\circ}_{m}}{kJ \cdot mol^{-1}}$	$\frac{T_{fus}}{K}$	$\frac{C_p(298.15K)}{J \cdot K^{-1} \cdot mol^{-1}}$
2O	87.07730[a]	0.200[b]	1.500[d]	0.9997 ± 0.0002[f,h]	16.29 ± 0.45 [f,h]	363.0 ± 0.2 [f,h]	113.8 ± 3.1 [f,h]
3A2O	129.11398 [a]	0.200 [b]	1.23 ± 0.03[e,g]	0.9970 ± 0.0009,[f,h]	15.34 ± 0.39 [f,h]	342.9 ± 0.5 [f,h]	164.7 ± 2.6 [f,h]
Cotton	28.50198 [a]	0.289 [c]	1.500[c]				46.94[c]

Standard uncertainty u is $u(P) = 1$ kPa.
[a] Molar masses are based on the 2011 IUPAC recommendations [10].
[b] Values taken from reference [11].
[c] Values taken from reference [12].
[d] Values taken from reference [13].
[e] Experimental value determined by measuring the mass and volume of a pellet of the compound at $T = 298.15$ K, standard uncertainties u is $u(T) = 0.5$ K.
[f] Experimental values obtained with the 2010 TA Instrument DSC calorimeter.
[g] The uncertainty is the standard deviation of the mean, which implies a standard uncertainty.
[h] The uncertainties are twice the overall standard deviation of the mean, and include the contributions from the calibration.