

Phase transitions study of the *o*-acetylnaphthol isomers by Calvet microcalorimetry

Vera L. S. Freitas, Paulo M. S. Sousa, Juliana A. S. A. Oliveira,
Maria D. M. C. Ribeiro da Silva

Centro de Investigação em Química (CIQ-UP), Department of Chemistry and Biochemistry,
Faculty of Sciences, University of Porto
Rua do Campo Alegre, S/N, P-4169-007 Porto, Portugal
e-mail: carlos.silva@fc.up.pt

The 1-acetyl-2-naphthol and 2-acetyl-1-naphthol isomers (Figure 1) form an intramolecular hydrogen bond (IMHB), due to the close relative position and orientation of the carbonyl oxygen towards the hydrogen of the hydroxyl group.¹⁻⁹ The formation of intramolecular hydrogen bonds (IMHB) in organic compounds can provide them photophysical properties with a multiplicity of applications in various scientific and technological domains. Generally, upon photo-excitation of compounds a fast acid-base reaction can occur via the IMHB resulting in a tautomeric transformation from the ground state enol form to an excited state keto form (excited state intramolecular proton transfer, ESIPT). Compounds who exhibit ESIPT phenomena are drawing considerable attention, due to their unique properties which facilitate novel optoelectronic applications, particularly focusing on chemical sensors, fluorescence imaging, proton transfer lasers, and organic light-emitting diodes (OLEDs); furthermore, they are also used as fluorescent probes of microenvironments in biological systems.

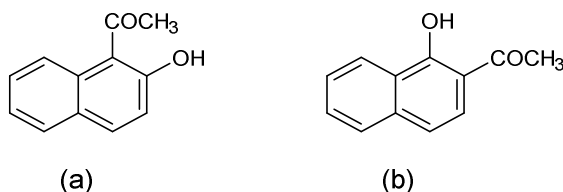


Figure 1. Structural formulae of 1-acetyl-2-naphthol (a) and 2-acetyl-1-naphthol (b).

Previous studies revealed that 2-acetyl-1-naphthol is thermodynamically more stable than 1-acetyl-2-naphthol isomer, both in the crystalline and gas phases.⁹

This presentation intends to continue with the energetic-structural characterization of these two isomers, with more focus on the energy of phase transitions (crystal-liquid, liquid-gas and crystal-gas). For this purpose, studies of sublimation, vaporization and fusion were carried out using a high-temperature Calvet microcalorimeter (Setaram HT1000, Lyon, France). A typical thermokinetic curve for these phase transition processes is depicted in Figure 2, where it can be seen that each calorimetric run is separated in two steps. In the first step, the heat flow relates to the process (cr, 298 K)→(l, $T_{\text{Calvet}} > T_{\text{fusion}}$) that involves heating of the crystal, its fusion, and heating of the resulting liquid. The second step begins with reducing pressure in the system which leads to the vaporization of the liquid (l, T_{Calvet})→(g,

T_{Calvet}). The sum of the two processes corresponds to the sublimation of the crystal (cr, 298 K) \rightarrow (g, T_{Calvet}).

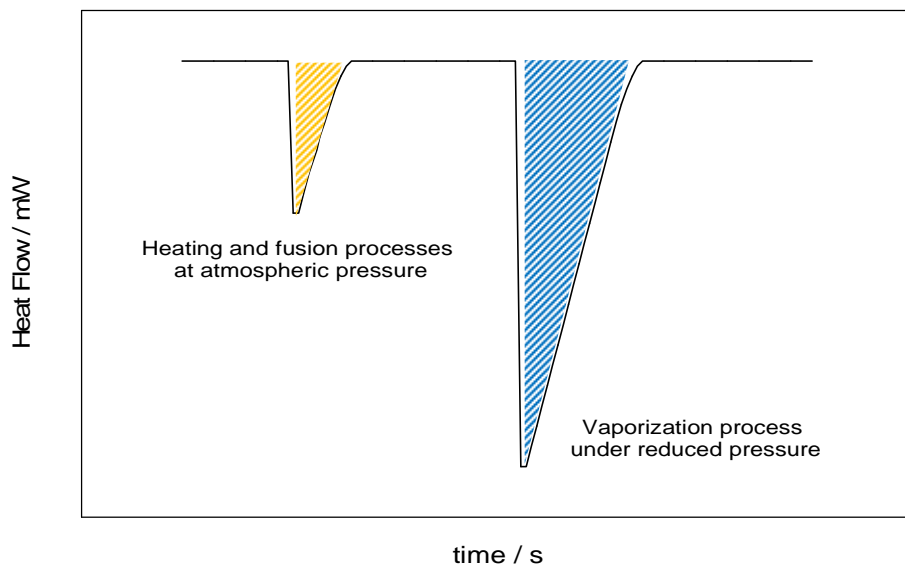


Figure 2. Typical thermokinetic curve for phase transition experiments using Calvet microcalorimetry (drop technique).

In this approach, the Calvet's working temperature, T_{Calvet} , has to be higher than the temperature of fusion of each compound.^{10,11} For this reason Differential Scanning Calorimetry (DSC) studies have also been carried out to obtain the fusion temperature of each isomer, as well as the fusion enthalpy at corresponding temperature.

The versatility of this approach using Calvet microcalorimetry for the combined energetic study of the three phase transitions of the *o*-acetylnaphthol isomers will be discussed. The results obtained will also contribute to a deeper understanding of the energy difference registered for the two isomers, of $27.7 \text{ kJ}\cdot\text{mol}^{-1}$.⁹

Acknowledgements: This work had the financial support of national funds, through FCT - Foundation for Science and Technology, Portugal, within the scope of the R&D project with reference UIDB/00081/2020. V.L.S.F thanks FCT and FCUP for the Program Contract established under the transition rule of Decree Law 57/2016, amended by Law 57/2017.

References:

1. J. Catalán, J.C. del Vane, Toward the photostability mechanism of intramolecular hydrogen bond systems. The photophysics of 1'-hydroxy-2'- acetonaphthone. *J. Am. Chem. Soc.* 115 (1993) 4321-4325.
2. A. Filarowski, A. Kochel, K. Cieslik, A. Koll, Steric and aromatic impact on intramolecular hydrogen bonds in *o*-hydroxyaryl ketones and ketimines. *J. Phys. Org. Chem.* 18 (2005) 986-993.
3. P.E. Hansen, S. Bolvig, K. Wozniak, Steric compression and twist in *o*-hydroxy acyl aromatics with intramolecular hydrogen bonding. *J. Mol. Struct.* 749 (2005) 155-168.

4. A.S. Al-Bogami, A.M. Al-Majid, M.A. Al-Saad, A.A. Mousa, S.A. Al-Mazroa, H.Z. Alkathlan, Cyclization of hydrazones of 2-acetyl-1-naphthol and 1-acetyl-2-naphthol with triphosgene. Synthesis of spiro naphthoxazine dimers. *Molecules* 14 (2009) 2147-2159.
5. Q. Su, X.-Y. Zhang, Y.-J. Zhang, L. Zhao, L. Wang, Y.B. Wang, Synthesis and supramolecular structure of 2-acetyl-1-naphthol. *Asian J. Chem.* 25 (2013) 5115-5116.
6. P. Schuster. *The Hydrogen Bond*, P. Schuster, G. Zundel, C. Sandorfy (Eds.) North-Holland, Amsterdam, The Netherlands, 1976.
7. S.J. Grabowski. *Hydrogen Bonding - New Insights. Challenges and Advances in Computational Chemistry and Physics*, Springer, Dordrecht, 2006.
8. M. Jablonski, Strength of Si-H \cdots B charge-inverted hydrogen bonds in 1-silacyclopent-2-enes and 1-silacyclohex-2-enes. *Struct. Chem.* 28 (2017) 1697-1706.
9. V.L.S. Freitas, M.D.M.C. Ribeiro da Silva, Structural and energetic insights on two dye compounds: 1-acetyl-2-naphthol and 2-acetyl-1-naphthol. *Molecules* 25 (2020) 3827.
10. A.R.R.P. Almeida, V.L.S. Freitas, J.I.S. Campos, M.D.M.C. Ribeiro da Silva, M.J.S. Monte. Volatility and thermodynamic stability of vanillin. *J. Chem Thermodyn.* 128 (2019) 45-5411.
11. M. Ledo, H. Flores, V.L.S. Freitas, J.M. Solano-Altamirano, J.M. Hernández-Pérez, E.A. Camarillo, F. Ramos, M.D.M.C. Ribeiro da Silva. Benzocaine: a comprehensive thermochemical study. *J. Chem. Thermodyn.* 147 (2020) 106119.