

**THERMODYNAMICS OF SUBLIMATION
OF INDOLINE BASED SPIROPYRANS
WITH DIFFERENT POSITIONS OF THE METHOXY GROUP**

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Spiropyranes are organic photochromic compounds used to create multifunctional materials such as optical filters, photoswitches, biosensors, and other hybrid materials. In this work thermodynamics parameters were studied at heterogeneous equilibrium for 1,3,3-trimethyl-6'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-22), 1,3,3-trimethyl-8'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-23), and 1,3,3-trimethyl-5'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-24).

The Knudsen effusion mass spectrometry was employed to obtain saturated vapor pressure and sublimation enthalpy. Since difference of structure of the compounds is the position of the methoxy group, the mass spectra of all spiropyranes are identical and has following main peaks: 159, 292, 307. The peak at m/z 307 corresponds to the molecular ion (M^+), 292 to $(M-CH_3)^+$, and the ion at m/z 159 results from the cleavage of the molecule at the spiro-atom. The vapor is monomolecular since dimers and trimers were not discovered in the mass spectrum.

Above the solids the saturated vapor pressures were determined by the Knudsen effusion method, which, in combination with mass spectrometric data, allow us to recommend the following equations for the temperature dependence of pressure for each of the compounds:

$$\text{SP-22: } \ln(p, \text{ Pa}) = (-15.95 \pm 0.19) \cdot 1000/T + (41.42 \pm 0.52), \quad \Delta T = 328\text{-}373 \text{ K}$$

$$\text{SP-23: } \ln(p, \text{ Pa}) = (-14.59 \pm 0.19) \cdot 1000/T + (38.25 \pm 0.57), \quad \Delta T = 322\text{-}348 \text{ K}$$

$$\text{SP-24: } \ln(p, \text{ Pa}) = (-14.13 \pm 0.09) \cdot 1000/T + (36.83 \pm 0.26), \quad \Delta T = 330\text{-}372 \text{ K}$$

The sublimation enthalpy was found using the second-law method of thermodynamics for the experimental temperature and recalculated to 298.15 K according to [1].

The thermodynamic data of sublimation

	$\Delta T, \text{ K}$	$T_{\text{hm}}, \text{ K}$	$\Delta_{\text{sub}}H^\circ(T_{\text{hm}}), \text{ kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{sub}}H^\circ(298.15), \text{ kJ} \cdot \text{mol}^{-1}$
SP-22	328-373	350	132.4±2.2	136.2±3.5
SP-23	322-348	335	121.3±2.1	124.1±2.9
SP-24	330-372	351	117.5±1.5	121.2±3.0

The first sample, in which the methoxy group is in the 6'- position, has the highest sublimation enthalpy. It correlates with the highest melting enthalpy and the lowest pressure among samples studied. The properties of SP-23 and SP-24 are similar.

1. Acree W.Jr., Chickos J.S. J Phys. Chem. Ref. Data. 2016. 45. 033101.

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