**Pyrazole derivatives as a potential liquid organic hydrogen carriers: evaluation of thermochemical data**

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**Highlights**

* Vapor pressures of alkyl pyrazoles measured by transpiration method.
* Vaporization enthalpies were derived and compared with the literature.
* Combustion experiments were performed on 1-methylpyrazole.
* Energetics of de(hydrogenation) reactions was discussed.

**1. Introduction**

Because of significant fluctuations in the daily power production and consumption of by the conventional and renewable energies, the development of new storage technologies for energy is necessary. Hydrogen is a very interesting option to overcome the drawbacks of other established storage options like *e.g*. storage under high pressures and very low temperatures. The reversible hydrogenation of liquid organic hydrogen carriers (LOHCs) is a new concept for a long-term storage of hydrogen. LOHCs can be efficiently used as an energy-carrying materials for mobile or stationary energy storage [1]. Generally, all unsaturated compounds could serve as hydrogen carriers. The hydrogenation of the LOHC is thermodynamically favorable [2-5]. An ideal LOHC is expected to possess the hydrogenation enthalpy at the level not higher than 40 kJ·mol-1/H2 [6]. This paper presents studies of thermochemical properties (enthalpies of formation and enthalpies of vaporization) for pyrazole derivatives that can be potentially used for hydrogen storage. A comparative thermodynamic analysis of the hydrogenation/dehydrogenation reactions was performed.

**2. Methods**

*Combustion calorimetry:* Standard molar energies of combustion of 2-methyl pyrazole was measured with a self-made high-precision isoperibolic calorimeter with a static bomb and a stirred water bath. The samples were placed (under an inert atmosphere in a glove-box) in polythene capsules and burned in oxygen at 3.04 MPa pressure.

*Transpiration method:* vapor pressure measurements. Vapor pressures of furfuryl alcohol and tetrahydrofurfuryl alcohol were measured using the transpiration method. About 0.5 g of the sample was mixed with small glass beads and placed in the thermostatted U-shaped saturator. A nitrogen stream with well-defined flow rate was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using the n-undecane as an external standard. The absolute vapor pressure *p*i at each temperature *T*i was calculated from the amount of the product, collected within a definite period.

*Computational details*. Quantum-chemical calculations have been performed with the Gaussian 09 series of programs. Energies *E*0 and enthalpies *H*298 of most stable conformers were calculated by using the composite G4-method.

**3. Results and discussion**

Experimental results are compiled in the tables below.

Thermochemical data at *T* = 298.15 K (*p°* = 0.1 MPa) for pyrazole derivatives (in kJ·mol-1)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | $∆\_{f}H\_{m}^{o}$(liq/cr) | $$∆\_{l,cr}^{g}H\_{m}^{o}$$ | $∆\_{f}H\_{m}^{o}$(g)exp | $∆\_{f}H\_{m}^{o}$(g)G4 |
| 1-methyl-pyrazole (liq) | 121.8±1.5 | 44.3±0.4 | 166.1±1.6 | 163.2±4.5 |
| 1-ethyl-pyrazole (liq) | 79.3±2.2 | 49.2±0.8 | 128.5±2.3 | 132.4±4.5 |
| 3-methyl-*1H*-pyrazole (liq) | 74.2±1.7 | 65.8±1.0 | 140.0±2.0 | 139.7±4.5 |
| 3,5-dimethyl-*1H*-pyrazole (cr) | 18.9±1.7 | 83.3±0.4 | 102.2±1.8 | 102.0±4.5 |
| 1,3,5-trimethyl-pyrazole (cr) | 19.9±2.0 | 73.1±1.3 | 93.0±2.4 | 86.5±4.5 |
| 1-benzyl-pyrazole (liq) | 202.8±2.1 | 72.0±0.8 | 274.8±2.3 | 270.2±4.5 |

Results from G4 calculations of thermodynamics of hydrogenation of pyrazole derivatives, at *T* = 298.15 K (*p°* = 0.1 MPa) in kJ·mol-1.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Compounds a |  | $∆\_{f}H\_{m}^{o}$(g) | $∆\_{f}H\_{m}^{o}$(g)c | $∆\_{r}H\_{m}^{o}$(g) | $∆\_{r}S\_{m}^{o}$(g) | $∆\_{r}G\_{m}^{o}$(g) | $Kp$(g) |
| 1-methyl-pyrazole | C4H6N2 | 163.2 | 110.2 | -47.9/24.0 | -254 | 27.8 | 1⸱10-5 |
| 1-phenyl-pyrazole | C9H8N2 | 289.6 | 40.8 | -239.3/47.8 | -608 | -57.8 | 1⸱1010 |

**4. Conclusions**

It has turned out that according to the calculated $∆\_{r}G\_{m}^{o}$(g, 298.15 K), that the hydrogenation of 1-methyl-pyrazole is thermodynamically not favourable, but in contrast the hydrogenation of 1-phenyl-pyrazole is very promising for the hydrogen storage with the large gas-phase equilibrium constant *Kp*(g) = 1⸱1010.

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