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Comprehensive study of the thermodynamic properties for 2-methyl-3-buten-2-ol

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ABSTRACT

The heat capacity of 2-methyl-3-buten-2-ol over the interval $T = (5$ to $370)$ K was measured in an adiabatic calorimeter. The standard entropy and heat capacity of the liquid phase at a reference temperature 298.15 K were found to be $S^{o}_{m} = (232.6 \pm 1.0)\ J \cdot K^{-1} \cdot mol^{-1}$ and $C_{s,m} = (237.4 \pm 0.9)\ J \cdot K^{-1} \cdot mol^{-1}$. The triple-point temperature $T_{fus} = (245.03 \pm 0.03)$ K and the corresponding enthalpy of fusion $\Delta^{l}_{cr}H^{o}_{m} = (5.199 \pm 0.012)\ kJ \cdot mol^{-1}$ were also determined. The enthalpy of vaporisation was determined with a Calvet-type calorimeter to be $\Delta^{g}_{l}H^{o}_{m}(305.1\ K) = (46.9 \pm 1.6)\ kJ \cdot mol^{-1}$. The vapour pressure over the temperature interval (280 to 328) K was measured with a static technique. The standard entropy of vaporisation at $T = 298.15$ K was found to be $\Delta^{g}_{l}S^{o}_{m} = (132.7 \pm 0.2)\ J \cdot K^{-1} \cdot mol^{-1}$. The standard enthalpy of combustion for liquid 2-methyl-3-buten-2-ol $\Delta_{c}H^{o}_{m}(l,\ 298.15\ K) = -(3145.1 \pm 2.7)\ kJ \cdot mol^{-1}$ was measured with two static-bomb isoperibol combustion calorimeters. From the experimental data, the standard enthalpies of formation for liquid and gaseous 2-methyl-3-buten-2-ol were found to be $\Delta_{f}H^{o}_{m}(l,\ 298.15\ K) = -(251.6 \pm 2.8)\ kJ \cdot mol^{-1}$ and $\Delta_{f}H^{o}_{m}(g,\ 298.15\ K) = -(203.3 \pm 2.8)\ kJ \cdot mol^{-1}$, respectively. The latter value was confirmed by high-level quantum chemical calculations. Molecular association in the gas phase and its effect on thermodynamic properties of the compound were discussed.

1. Introduction

2-Methyl-3-buten-2-ol ($C_5H_{10}O$, CASRN 115-18-4) is one of the volatile organic compounds that are important in atmospheric chemistry, especially as precursors of tropospheric ozone [1,2]. For example, this compound was shown to account for approximately 20% of local OH reactivity in the Sierra Nevada Mountains in the day-time [3]. The main emitters of 2-methyl-3-buten-2-ol seem to be pine species [4]. Though only a limited number of plant species investigated emit 2-methyl-3-buten-2-ol, its emission may play an important role in regional photochemistry and could contribute a significant amount of acetone to the atmosphere [5]. On the other hand, this natural unsaturated alcohol, which is intensively emitted by pine needles, is one of two principal aggregation pheromone components of a spruce bark beetle, *Ips typographus*, aiding identification of sick trees by the beetle [6]. 2-Methyl-3-buten-2-ol is used mainly as a starting material or intermediate in the synthesis of medical drugs, vitamins A and E, and perfumes [7].

Available thermodynamic properties for the compound are limited to the vapour pressure [7–14], liquid heat capacity [7,8], and enthalpy of formation [15]. As demonstrated below, the available vapour–pressure data are inconsistent. In addition, such a flexible molecule with an –OH group is of intrinsic interest due to the possible mutual effects of rotating tops and hydrogen bonding. The latter results in molecular association in both the liquid and gas phases.

In this work, we report results of an experimental study of the thermodynamic properties of 2-methyl-3-buten-2-ol, including heat capacity in the condensed phases, temperatures and enthalpies of phase transitions, and enthalpies of combustion and formation in the liquid and gaseous states. Quantum chemical and statistical thermodynamic calculations are used to verify the gas-phase thermodynamic functions and to assess the effect of the molecular association on the reported properties.

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