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Thermodynamic study of solvent-free reaction between 17-methyltestosterone and o-aminophenol

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ABSTRACT

In this work we investigated the possibilities of the solvent free synthesis of Schiff base (azomethyne) from 17-methyltestosterone and o-aminophenol. The study of the binary mixtures of 17-methyltestosterone and o-aminophenol was achieved by DSC, TG–DSC, and FTIR. The isolated compounds and reaction product were studied by adiabatic bomb calorimetry in order to determine the heat of reaction. The DSC data reveal a simple eutectic followed by a chemical reaction in liquid phases. From the DSC data we calculated the enthalpy of decomposition of reaction product as $(44.65 \pm 0.83)\ \text{kJ} \cdot \text{mol}^{-1}$. Schiff base formation by condensation reaction was highlighted by TG–DSC method and the structure of the solid product was confirmed by FTIR spectroscopy. The standard enthalpy of reaction was calculated from the standard molar enthalpy of formation of reactants and products.

1. Introduction

Schiff bases derived from aromatic amines and aromatic aldehydes or ketones have a wide variety of applications in many fields, *e.g.*, biology, medicine, and chemical industry [1]. Unfortunately, most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria like: tautomeric interconversions, hydrolysis, or formation of ionized species [1,2]. Thus in non-polar solvents enolimine was predominantly present, while in polar solvents rapid tautomeric interconversion of enolimine to ketoamine and slow hydrolyses are present [3]. The final molecular structure and yields of the reaction product depend on the reaction condition. From this point of view it is advantageous to obtain Schiff bases by a solvent free synthesis because such reactions occur more efficiently and with more selectivity compared to the reactions carried out in solvents [4–6].

Solvent-free organic syntheses are very important from the point of view of green chemistry [7]. The reactions between solids can be classified into: solid phase synthesis (the reaction of molecules from a fluid phase with a solid substrate); solvent-free synthesis (any system in which neat reagents react together, in the absence of a solvent); and solid state synthesis or solid–solid reactions (two macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or a vapor phase [6]).

In this work, we investigated the possibilities of the solvent-free synthesis of Schiff base from 17-methyltestosterone and o-aminophenol.

In this binary mixture the reaction takes place in the liquid phase. This liquefaction implies the existence of a eutectic mixture with a melting temperature below the melting temperatures of pure components.

The reaction was carried out directly in a thermoanalytical apparatus (TG, DSC) by introducing 1:1, 1:2, and 2:1 molar ratio mixtures into the pans.

In order to determine the structure the solid reaction products were studied by FTIR spectroscopy.

The heats of reaction were calculated from the heat of formation of reactants and products. The heats of combustion have been determined using an adiabatic bomb calorimeter.

2. Experimental

2.1. Materials

17-Methyltestosterone (Merck, melting temperature from (434 to 439) K and purity 0.99 mass fraction) and o-aminophenol (Merck, melting temperature from (443 to 447) K and purity 0.995 mass fraction) were used without further purification. The 1:1, 1:2, and 2:1 molar ratio mixtures were prepared by weighing and grinding together at room temperature.

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TABLE 1
Melting temperatures, enthalpy of fusion, and entropy of fusion of pure components.

Pure compound	T_{fus}/K		$\Delta_{fus}H$/(kJ · mol^{-1})		$\Delta_{fus}S$/(J · mol^{-1} · K^{-1})	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
17-Methyltestosterone (17MT)	437.34 ± 0.31	438.00 [13]	25.02 ± 0.22	25.70 [13]	57.20 ± 0.47	57.90
o-Aminophenol (oAF)	448.72 ± 0.43	447.40 [14]	26.74 ± 0.51	25.40 [15]	59.58 ± 1.08	

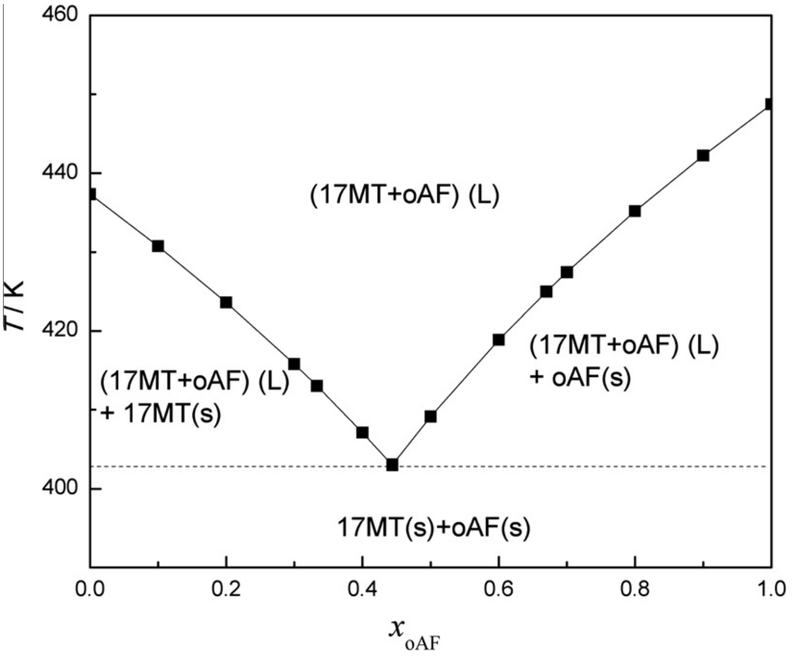

FIGURE 1. Ideal solid–liquid phase diagram for binary mixture (17-methyltestosterone + o-aminophenol).

2.2. Methods

All samples were characterized by DSC, TG, FTIR, and combustion calorimetry.

The transition temperature and enthalpy of transition were determined by differential scanning calorimetry (Perkin Elmer Diamond DSC) under a heating rate of 10 K/min over a temperature range from (323 to 573) K. The apparatus was calibrated for temperature and enthalpy by melting high purity indium. The instrument was flushed with argon. Samples of 2 to 4 mg were transferred into aluminum pans which were sealed and weighed with the Partner XA balance with a precision of 10 µg.

The water loss and the thermal behavior were determined with a simultaneous TG–DSC NETZSCH STA 409 thermoanalyzer under a heating rate of 10 K/min over a temperature range from (323 to 773) K in a nitrogen flow. Samples of 3 to 8 mg were transferred into Pt–Rh pans.

The infrared spectra were obtained from KBr pellets, using a Vertex 70-Bruker spectrophotometer (4000 to 400) cm^{-1}.

The heat of combustion (internal energy change, ΔU) was measured in an oxygen bomb combustion calorimeter model Gallenkamp CB-110. The bomb calorimeter and technique have been described previously [8]. The sample was pressed into pellets and suspended with a cotton string in a small sample crucible. The sample was burned with 1.00 cm^3 of water introduced into the bomb. The bomb was purged twice to remove air, before being charged with $p = 2.53$ MPa of oxygen. Ignition was achieved using a cotton string by a Ni–Cr wire, for both of which the thermochemical characteristics were known (0.853 J · cm^{-1} for Ni–Cr wire and 17489.12 J · g^{-1} for cotton string) [9]. The calorimeter temperature was registered with a chromel-alumel thermocouple (type K) with a tolerance class one ±1.5 K, calibrated according to IEC 584/1995. The voltage of the thermocouple was measured with a $6\frac{1}{2}$ digits multimeter (Keithley 2700) connected to a PC. Data acquisition has been performed with a TestPoint program. The temperature measurement resolution was 10^{-3} K. After combustion, the gas mixture from the bomb was evacuated and the wall and accessories were washed with bidistilled water. This solution was titered with 0.1 N NaOH solution, using methyl orange as an indicator. Correction for nitric acid formation was based on -59.7 kJ · mol^{-1} for the molar energy of formation of 0.1 mol · L^{-1} HNO_3(aq) from N_2, O_2, and H_2O(L) [10].

The standard state ($T = 298.15$ K and $p = 101.325$ kPa) correction were calculated with Washburn equation recommended in case of compounds with carbon, hydrogen, and oxygen [11]. The equation applies fairly well in the case of nitrogen compounds as well [12].

The energy equivalent of the calorimeter, ε_{calor}, has been determined using about 0.6 g of benzoic acid (Riedel de Haen AG Seelze Hannover 8E 80409) with a massic energy of combustion of $\Delta_c u = -(26434 \pm 3)$ J · g^{-1}. The calibration results were corrected to give the energy equivalent ε_{calor} corresponding to the average mass of water added to the calorimeter 2092.0 g. One set of six calibration experiments were performed leading to the value of