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Green and conventional synthesis of sulfanilic acid

Research article

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Abstract
Synthesis of sulfanilic acid was achieved by conventional and green protocols. The starting reagents were the same in both methods. The activation technique of the reaction was different. Conventional synthesis was thermally activated and green synthesis was activated by microwaves. Energophage, chronophage and polluting features constitute important disadvantages of conventional method. The green method performs much better than the conventional procedure: short time, few hazardous wastes and easy experimental setup. The zwitterionic structure of the sulfanilic acid was demonstrated by spectroscopy.

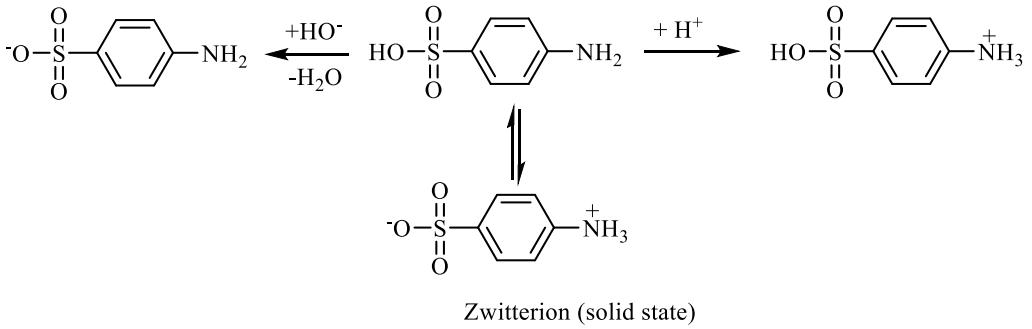
Keywords: sulfanilic acid; microwaves; thermal activation; aniline; spectroscopy.

1. INTRODUCTION

Sulfanilic acid or 4-aminobenzenesulfonic acid is one of the most widely used organic compounds with mixed functions in the synthesis of azo dyes, color additives, pesticides and pharmaceutical perfumes [1].

Sulfanilic acid is a white-gray solid, cheap, environmentally friendly and very chemically stable. Its melting point is 288° C, the acidity is *pKa* of 3.23 (in water) and water solubility is 12.5 g/L. Its acidity (*pKa* of 3.23 in water) is higher than that of benzoic acid (*pKa* of 4.2) and acetic acid (*pKa* of 4.8), but it is much lower than that of *p*-toluene sulfonic acid (*pKa* of −2.8) and of methane sulfonic acid (*pKa* of −2) [2].

The solid phase of sulfanilic acid exists as zwitterion. The $–NH_2$ (amine) and $–SO_3H$ (sulfo) groups provide amphiprotic properties of the sulfanilic acid molecule (Scheme 1).



Scheme 1. Sulfanilic acid structures in solid state and aqueous solution [3]

The zwitterionic property of sulfanilic acid is responsible for the excellent catalytic properties of this compound in the green chemistry like environmentally solvent-free phase transfer catalysis [3]. This compound was used as organocatalyst in synthesis of 4-arylidene-3-substituted isoxazole-5(4H)-ones [4], green synthesis of quinoxaline derivatives [5], one-pot three-component Mannich reaction for the synthesis of β-amino ketone [3], and solvent-free synthesis of 1,5-benzodiazepine derivatives [6].

Sulfanilic acid is the raw material for the synthesis of many organic dyes by the diazotization reaction to diazonium salt, 4-diazoniobenzenesulfonate, followed by the coupling reaction with phenols or aromatic amines. 4-Diazoniobenzenesulfonate is also a zwitterion, a stable precipitate in aqueous medium with a melting point of 104 ° C, used to obtain a large number of azo dyes [7-9].

Sulfanilic acid and N- (1-naphthyl) ethylenediamine are the two components of the Griess reagent. The Griess test detects the nitrite anion in drinking water. Peter Griess is the German chemist who discovered it in 1858 [10]. The Griess reagent is based on the diazotization reaction of sulfanilic acid by nitrite ions followed by the coupling of the diazonium salt with N- (1-naphthyl) ethylenediamine to form pink-red azo dye which absorbs at 548 nm [11].

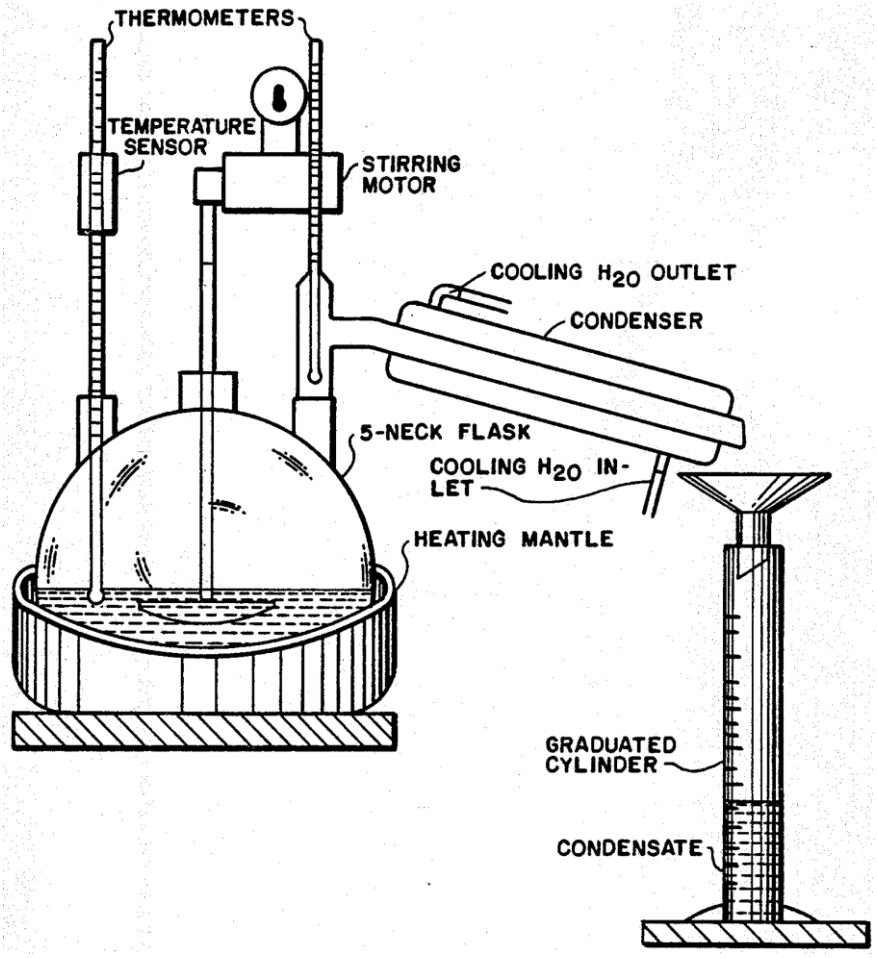


Figure 1. A lab-scale batch reactor for sulfanilic acid synthesis [12, 13]

Conventional industrial synthesis takes place by so-called baking process at very high temperatures 180-190° C in concentrated sulfuric acid which is also the reaction medium [12]. A pilot laboratory installation is shown in Figure 1.

Green chemistry or sustainable chemistry aims at the synthesis of organic compounds by processes that do not cause alteration of the environment. One of the green methods is to perform organic reactions using microwaves [14, 15].

In Romania, I am the researcher who published the first scientific article on the use of electromagnetic microwaves in chemical reactions. The article was published in the "Revue Roumaine de Chimie" in 1998 [16]. This was part of a research project completed with the first cotutelle doctoral thesis in the history of Romania and France [17]. The doctoral research grant was won in the competition organized by the Romanian Ministry of Education and awarded by order of the Romanian Minister of Education no. 7256 of 15.09.1994. We have shown that in the reaction medium, irradiated with microwaves, hot spots are formed, which are similar to catalytic centers, and can activate the reaction [18]. Using our precedent knowledge [17, 19], we intended to synthesize sulfanilic acid by a clean method with the help of microwaves.

2. MATERIALS AND METHODS

2.1. Materials

Aniline and sulfuric acid are commercial compounds from Sigma-Aldrich.

2.2. Apparatus

Ultraviolet-visible spectra were recorded in water solution using a Cary 50 UV-Vis spectrophotometer. Infrared spectra were recorded using an Alpha Bruker Optics spectrometer in the range of 500-4000 cm^{-1}. The melting points were determined on a Gallenkamp digital melting point apparatus. A commercial microwave oven (2450 MHz, 400 W) was employed. The structure of the sulfanilic acid was confirmed by comparing its physical properties (melting temperature, IR absorption

bands, UV-VIS bands) with those of the known compound from the literature.

2.3. Methods

a. Procedure for the conventional synthesis of sulfanilic acid

Pour into a 15 mL porcelain crucible 2.5 mL (2.555 g; 27.5 mmol) of aniline and gradually 2.5 mL of 96% sulfuric acid (4.6 g; 47 mmol; ρ= 1.84 g/mL) and mix with a thermometer. The neutralization reaction is exothermic. Heat slowly the solid-liquid heterogeneous mixture of the porcelain crucible on a sand bath until the temperature reaches 190°C, when the water has evaporated and the reaction medium becomes solid. Then heat the aniline salt formed for 4 hours at 200 °C. Allow to cool the resulting mixture and pour it into a beaker with 25 mL of 10% Na_2CO_3 on heating. Add activated charcoal, boil for a few minutes, filter hot and acidify with hydrochloric acid the solution of sodium sulfanilate. The sulfanilic acid crystallizes out from the filtrate after standing overnight. The resulting crystals are filtered and dried in an oven at 105 °C. Yield 80%.

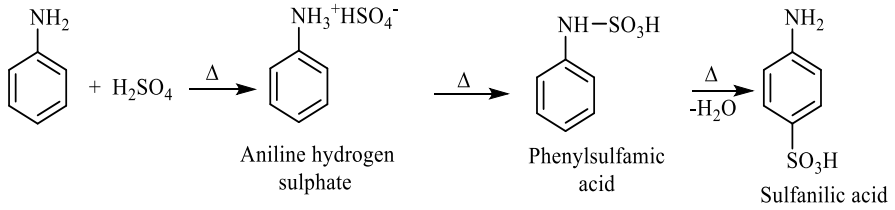
Sulfanilic acid. mp. 288°C; molecular formula $C_6H_7NO_3S$; UV-VIS: 248 nm, 294 nm; IR: 2857w, 2630 w, 1629vw, 1574w, 1545w, 1498m, 1422vw, 1318vw, 1242s, 1153vs, 1109vs, 1032vs, 1007vs, 829m, 683vs, 569vs.

b. Green synthesis of sulfanilic acid

In a 15 mL porcelain crucible was introduced 0.25 mL of aniline (0.255 g; 2.7 mmol) and gradually 0.23 mL of 96% sulfuric acid (0.423 g; 4.32 mmol; ρ=1.84 g/mL). The resulting paste of aniline hydrogen sulfate was irradiated in a microwave oven (2450 MHz) for 3 minutes at 400 W. The reaction mixture is poured into a 25 mL glass beaker with 10 mL cold ice-water. The crystals of sulfanilic acids are filtered off, recrystallized from water and dried in an oven at 105 ° C. Yield 90%.The product is identical to the one obtained through conventional synthesis.

3. RESULTS AND DISCUSSION

The synthesis of sulfanilic acid proceeds according to the following reaction scheme, starting from aniline and sulfuric acid (Scheme 2).



Scheme 2. Sulfanilic acid synthesis

The reaction between aniline and sulfuric acid is exothermic and rapidly. The resulting aniline hydrogen sulfate melts at 160 ° C and its conversion to phenylsulfamic acid and sulfanilic acid takes place endothermically at 180-200°C. Sulfanilic acid is stable in the reaction medium and decomposes at 288°C. Conventional synthesis of sulfanilic acid requires over 4 hours in drastic experimental conditions. The temperature of the reaction medium is about 200 °C. At this temperature the reaction occurs in the melt. Recovery of the product from the reaction medium is done by neutralization with sodium carbonate to the salt of sodium sulfanilate *p*-H_2N-C_6H_4-SO_3Na. The latter is transformed into sulfanilic acid by acidification with hydrochloric acid. The conventional method is cumbersome. That is why we set out to achieve an easier method of sulfanilic acid synthesis.

Electromagnetic microwaves are a green way of activating organic chemical reactions. The use of microwaves in the synthesis of sulfanilic acid is possible because the reaction medium is polar and absorbs electromagnetic radiation. The dipole moment of aniline is μ=1.53 D, and that of sulfuric acid is μ=2.96 D. Moreover, the reaction medium is pasty, and hot spots can be easily created inside it [15-17]. The heterogeneous medium, aniline hydrogen sulfate paste, was irradiated at 400 W and different reaction times. The best result is obtained after 3 minutes. An increase in irradiation time does not increase the yield, but decreases it. This is explained by the formation of by-products in the reaction medium. A small excess of aniline helps

increase the yield of the synthesis, aniline being the nucleophile and sulfuric acid the electrophilic reagent. Unconventional synthesis of sulfanilic acid using microwaves quickly provides the product and is environmentally friendly.

The ultraviolet-visible spectrum of sulfanilic acid exhibits two absorption bands (Figure 2). The first band appears at 248 nm and is intense. The second band shows a shoulder at 294 nm and is also due to a transition. Both UV-VIS bands are assigned to $\pi \rightarrow \pi^*$ transitions.

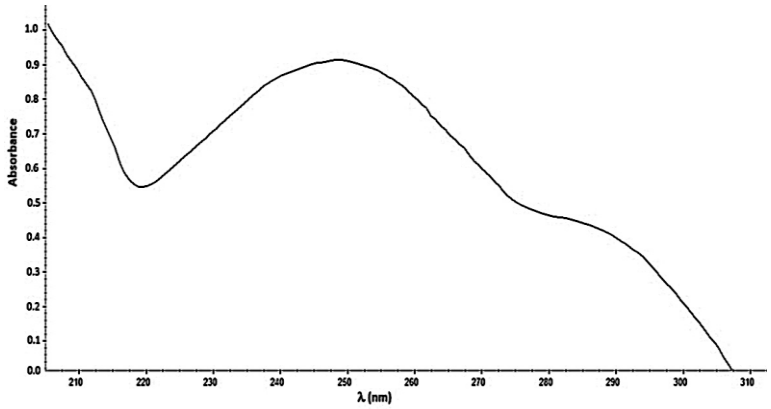


Figure 2. UV-VIS spectrum of sulfanilic acid in water

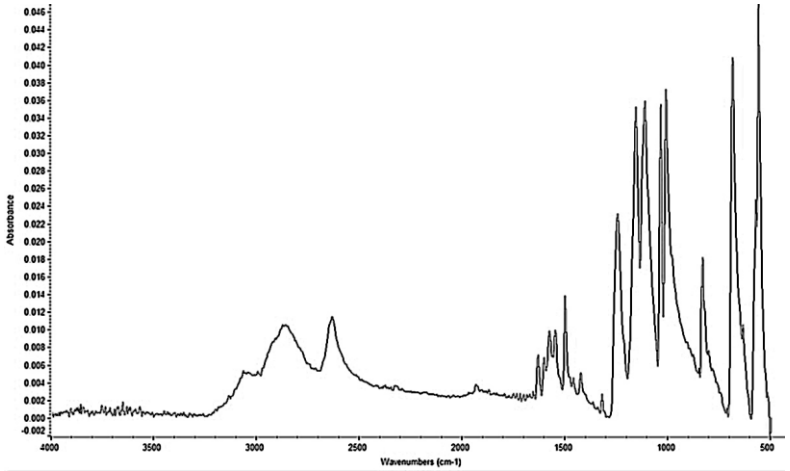
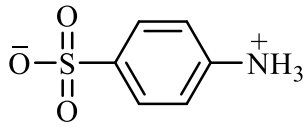


Figure 3. IR spectrum of sulfanilic acid

Infrared spectroscopy is used to find structure of a compound. The spectrum of sulfonic acid (Figure 3) does not exhibits bands due to -SO_3H, -NH_2, and -OH functions. But it shows absorption for ammonium

group -$^{+}NH_3$ and sulfonato group-SO_3^-. Ammonium group reveals a weak stretching band at 2857 cm^{-1}. Sulfonato group [20] exhibits absorption bands at: 1242 cm^{-1}(very strong intensity) and 829 cm^{-1} (medium intensity). Characteristic benzene ring stretching vibrations [21] peaking occurs at 1498 cm^{-1} (medium intensity). The ring C-H stretching vibration exhibits at 3063 cm^{-1} (very weak intensity). The infrared peaking at 1851 cm^{-1} belongs to C=C absorption (very weak intensity). C–H in plane bending displays at 1032 cm^{-1} (very strong intensity) and C–H "oop" (out-of-plane) bending appears at 683 cm^{-1} (very strong intensity). These IR bands demonstrate zwitterion structure of the compound:



Sulfanilic acid

4. CONCLUSION

Synthesis of sulfanilic acid can be accomplished by conventional or unconventional methods. The conventional approach engages an energophage, chronophage and polluting process.

A green method has been implemented involving microwave activation. The unconventional protocol is superior to the conventional one both in terms of reaction time and yield. The experimental installation is simplified and the working conditions are easy.

In addition, the unconventional method is environmentally friendly.

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