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Fig. 2. Absorption spectra of aqueous solutions of 4-chloro-2-sulfobenzalacetophenone (I) and its sodium salt (II)

Figure 2: Fig. 2. Absorption spectra of aqueous solutions of 4-chloro-2-sulfobenzalacetophenone (I) and its sodium salt (II)

Abstract

Full Text

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ON CERTAIN OPTICAL PROPERTIES OF 4-CHLORO-2-SULFOBENZALACETOPHENONE

(Presented by Academician B. A. Kazanskii, July 3, 1964)

In the course of studying sulfo derivatives of chalcones, we noticed a change in the color of the powder of 4-chloro-2-sulfobenzalacetophenone (I) upon drying.

Cl – benzene ring – CH=CH – CO – benzene ring SO_3H (I)

Whereas the aqueous solution of the sulfonic acid and its powder in the moist state are almost colorless, a well-dried powder is intensely yellow, a color that rapidly disappears in the presence of moisture. Sodium salt I is almost colorless even in the dried state. A similar phenomenon, as is known, is observed when various ketones, including chalcones, are dissolved in concentrated sulfuric acid. In this case the absorption bands

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shift considerably into the long-wavelength region; upon dilution of sulfuric-acid solutions with water, the original coloration is restored (^{1}).

This prompted us to investigate in greater detail the spectral characteristics of I and of its sodium salt.

The absorption spectra of I in methanol and in concentrated sulfuric acid are very close to the spectra of 4-chlorobenzalacetophenone, which contains no sulfo group (Fig. 1). The absorption spectra of aqueous solutions of I and of its sodium salt are also very close to one another (Fig. 2). The fact that, on drying, the sodium salt remains almost colorless makes it possible to suppose that the intense yellow color of the dried powder of the free sulfonic acid is connected with an interaction of the carbonyl and sulfo groups.

As follows from measurement of the IR spectra of 4-chlorobenzalacetophenone, I, and the sodium salt of I, in 4-chloro-2-sulfobenzalacetophenone, by comparison with the other two substances, the frequencies of the stretching vibrations of the carbonyl group are shifted by ~ 20 cm^{-1} toward lower frequencies, i.e., by an amount characteristic of substances in which the carbonyl group participates in an interaction of the hydrogen-bond type.

This interaction may occur both within a single molecule and between two or several molecules of the sulfoketone. The latter assumption seems more probable to us.

In benzalacetophenone-2-sulfonic acid, analogous properties are expressed much more weakly than in the corresponding 4-chloro-substituted compound. In all probability, chlorine increases the mobility of the hydrogen atom of the sulfo group, thereby facilitating the formation of a hydrogen bond or the transfer of a proton to the oxygen of the carbonyl group, the possibility of which is also not excluded.

4-Chloro-2-sulfobenzalacetophenone was obtained by us as follows: to a solution of 6 g of caustic soda in 80–85 ml of 30% ethanol, with vigorous stirring, 12 ml of acetophenone is added, and then 29 g of sodium 4-chlorobenzaldehyde-2-sulfonate is introduced in small portions. The solution remains transparent, and then, almost instantaneously, a precipitate of the sodium salt of 4-chloro-2-sulfobenzalacetophenone separates. The precipitate is filtered off, washed on the filter with ice water, and recrystallized from 500 ml of water.

The sodium salt is a crystalline precipitate in the form of colorless, lustrous needles; it does not melt. Yield 28 g (75%). The sodium salt is converted into the free acid by adding concentrated hydrochloric acid (25–30 ml) to an aqueous solution (or suspension) of the salt; after 15–20 min the precipitate of sulfonic acid is filtered off, washed on the filter with ice water, recrystallized twice from water (200–250 ml each time), and dried at 70–80°; in the process the substance assumes an intense yellow color. Yield 17–18 g (48–50%); m.p. 187–188°.

Found, %: Cl 10.75, 10.83
$C_{15}H_{11}O_4ClS$. Calculated, %: Cl 11.01

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