p-DIMETHYLAMINOAZOBENZENE-p-SULFONAMIDE

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In the course of an investigation the compound p-dimenthylaminoazobenzene-p-sulfonamide was prepared and it was decided to study some of its properties. Its close similarity to methyl orange suggested its possible use as an indicator. The structure of the two compounds is identical except for the amide group replacing the OH group found in methyl orange.

Examination of the literature reveals that p-dimethylaminoazobenzene-p-sulfonamide was prepared in Russia in 1938[1]. The investigators prepared a number of azo compounds by the same general method here used, but they were interested primarily in the therapeutic values of the compounds. The common physical properties were not included in their report.

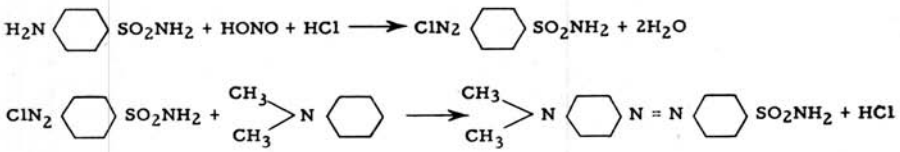
EXPERIMENTAL

17.2 gm. of p-aminobenzenesulfonamide are dissolved in 150 ml. of water containing 25 ml. of concentrated HCl; 12.6 gm. of dimethyl aniline are dissolved in 20 ml. of concentrated HCl and the solution diluted with about 200 ml. of water; 6.9 gm. of $NaNO_2$ are dissolved in about 15 ml. of water. The three solutions are then cooled in an ice-water mixture. The solution of $NaNO_2$ is added to the p-aminobenzenesulfonamide and thoroughly stirred. The resulting diazonium salt is then slowly poured into the dimethylaniline, stirring constantly. The solution first becomes orange and gradually changes to a deep red. Crystals appear in about ten minutes. The solution is further stirred for about ten to fifteen minutes and allowed to stand for an hour. The precipitate is filtered with suction and washed with water. The yield is almost quantitative.

The crystals are small, well defined and purplish-red in color. The compound is practically insoluble in water, benzene, and ether; somewhat soluble in acetone, methyl and ethyl alcohols; and still more soluble in ethylene glycol. Upon heating, the compound decomposes at about 188 to 195° C. before melting.

An approximate determination of the pH at which the dye changes color showed the range to be about between a pH of 3 and 4.5. A series of buffer solutions was made between a pH of 3 and 4.6 in steps of 0.2 of a pH unit using the directions of Clark and Lubs and mixing the proper amounts of 0.1 M $KHC_8H_4O_4$ and 0.1 N HCl and 0.1 N NaOH. The pH values of these buffers were then measured electrometrically using a glass and calomel electrode, and the differences between the calculated and measured values were only 0.01 to 0.02 of a unit.

After trial with numerous solvents, a 0.1 percent solution of the dye in ethylene glycol was made and used; 0.15 ml. of this solution were added to 10 ml. of each buffer and the colors were observed and compared with those produced using methyl orange as an indicator. The pH intervals for the two indicators were found to be almost identical; 3.2 to 4.2 for methyl orange, and 3.0 to 4.2 for the sulfonamide. The



[1] L. N. Goldyrev and I. Ya Postooskii, J. Applied Chem. (USSR) *11*, 316-27, (1938).

point of greatest change for methyl orange seemed to occur between a pH of 3.4 and 3.6 while that for the sulfonamide was about 0.2 of a unit higher, 3.6 to 3.8.

The sulfonamide as used in the above tests tended to precipitate when added to the buffer solutions, and the colors produced were not as deep as those obtained using methyl orange. The color change offered one advantage, however; it was from red to yellow with practically no orange in between.

The color intensity obtained with methyl orange is due to the fact that it is a water-soluble sodium salt of a weak acid, whose behavior in acid and basic solutions is well postulated. The water insolubility of the sulfonamide and the presence of the amide group instead of the acid OH group may explain the faint colors produced, but the nature of the compound also presents a mechanism in acid and basic solutions which is not clear. It seems that the introduction of another sulfonic group might overcome this difficulty. This, of course, may change the indicator interval and also its colors, and this possibility may be investigated in the future.