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Note

Persulphate ion as a reagent for the detection of aromatic compounds containing the NH_2 group using thin-layer chromatography

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The persulphate ion is one of the oxidizing agents known in aqueous solution and has been used in the oxidation of a large number of organic compounds during the last few decades. During the systematic study of the oxidation of organic aromatic compounds by persulphate ions it was noticed that such compounds (*i.e.*, aromatic amines, phenols and other related compounds) either gave coloured precipitates or solutions on oxidation[1]. Taking advantage of this visible effect, an aqueous persulphate–silver nitrate mixture was used as the spray reagent for the identification of few aromatic amines and other related compounds separated by thin-layer chromatography (TLC) or paper chromatography [2–4]. While Bertetti[5] used a $K_2Cr_2O_7$ solution acidified with sulphuric acid as a spraying reagent for identification of amines, Kitahara and Hiyama[6] used 1-naphthol-4-sulfonic acid. In the present investigation we used a $K_2S_2O_8$–$AgNO_3$–acetone–water mixture on other aromatic compounds separated by TLC. Thus in the present note we describe the results obtained by using the above mixture as a spray reagent on few pyridine derivatives and other compounds separated by TLC.

EXPERIMENTAL

Analar grade certified $K_2S_2O_8$ and silver nitrate were used (Fisher Scientific, Pittsburgh, PA, U.S.A.). All compounds studied were recrystallized from samples which were either C.P. or Analar grade Fisher or Aldrich (Milwaukee, WI, U.S.A.) chemical. The solvents were checked for purity and distilled if necessary.

Spray reagent

A solution of $K_2S_2O_8$, $AgNO_3$ and acetone in distilled water was used. The total concentration of the compounds were as follows: $K_2S_2O_8$ (1.0%, w/w), acetone (2%, v/v) and $AgNO_3$ (0.002 *M*).

Apparatus

The apparatus was similar to the one used by us previously[2]. A glass tank (28 × 26.5 × 9 cm) was used to separate pyridine derivatives and amino compounds. Silica gel GF (Analtech, Newark, DE, U.S.A.) plates were employed. No special temperature control was used; the laboratory temperature was 20 ± 5°C.

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Method

The TLC plates were first heated at 100°C for 1 h to remove water, etc., in an oven. The solution of studied compounds (0.05 %) in acetone–water (1:1) was spotted on the silica gel TLC plates, at equal distances, 1 in. above the bottom edge of the plate, by the use of a fine capillary tube. The spots were allowed to air dry or were dried with an air blower. The upper layer from the butanol–acetic acid–water (50:10:40) mixture was placed in the tank. The tank was covered and left for 2 h for equilibrium to be reached between the vapour and liquid phase. The plates were held in the tank so that the spots were ≈ 2 cm above the surface of the solvent. The chromatograms were developed until the solvent front had moved to ≈ 1 in. from the upper edge of the plate. Development took *ca.* 5 h. The plates were removed from the tank and the solvent front was marked. The solvent was removed by evaporation by keeping the plates at room temperature or by blowing air over them. The spot locations were determined by spraying the plates with the spraying reagent (see above). The coloured spots appeared either at room temperature or upon cooling the plates for 15 min after heating for 5 min at 50°C in an oven after first treating the plates with the spraying reagent.

RESULTS AND DISCUSSION

Observations regarding the spot colour, sensitivity, and the R_F values are given in Table I. With this procedure we successfully separated and identified amines,

TABLE I

R_F VALUES AND COLOUR REACTIONS OF AMINES, PHENOLS, ETC., WITH A PERSULPHATE–SILVER NITRATE–ACETONE MIXTURE

Compound	*Colour of the spots*	*R_F in butanol–acetic acid–water (50:10:40)*	*Smallest detectable amount (μg approx.)*
m-Aminobenzoic acid	Yellow	0.84	0.6
p-Aminobenzoic acid*	Dark yellow	0.89	0.3
2-Aminopyridine	Yellow	0.61	0.4
3-Aminopyridine	Yellow	0.57	0.4
4-Aminopyridine	Yellow	0.51	0.4
2-Amino-4-nitrophenol*	Yellow	0.91	0.3
2-Aminothiazole	Yellow	0.58	0.3
2-Aminobenzamide	Yellowish brown	0.85	0.4
4-Aminosalicylic acid	Dark yellow	0.85	0.5
8-Aminoquinoline*	Pink yellow	0.87	0.6
o-Aminophenol*	Black	0.78	0.3
Anthranilic acid*	Dark yellow	0.93	0.5
Indole	Violet	0.96	0.4
3,3-Diaminobenzidine*	Violet	0.49	0.3
p,p-Biphenol	Green	0.90	0.8
2-Biphenylamine	Brown	0.89	0.7
Pyrene	Brown (tailing)	0.91	0.9
m-Dinitrobenzene	Brownish black	0.94	0.4
Hydroquinone*	Pink	0.90	0.6

* Spot at room temperature.

pyridine derivatives and other related compounds and obtained beautiful spots. While *o*-aminophenol, 3,3′-diaminobenzidine, 2-amino-4-nitrophenol, *p*-aminobenzoic acid and anthranilic acid gave coloured spots at room temperature, others gave coloured spots on heating. However, this depended on the concentration of the compounds. It may be noted from the table that the R_F values of aminopyridines decreased with an increase in the position number (*i.e.*, 2, 3 and 4) of the NH_2 group in the pyridine ring. We successfully separated and identified indole (benzopyrrole). It was also observed that a compound containing a NH_2 group in the *para* position (*p*-aminobenzoic acid, diaminodiphenylamine, etc.) gave a sharp and bright spot at once when sprayed with the above mentioned spraying reagent. The presence of acetone in the spraying regeant increases the sensitivity for identification of compounds like sulfapyridine, etc., which are less soluble in water.

Thus satisfactory results were obtained by using a $K_2S_2O_8$–$AgNO_3$–acetone–water mixture as a spraying reagent for the identification of aromatic amino compounds, pyridine derivatives, indole, etc., by using solvents like benzene–methanol, benzene, chloroform, or butanol–acetic acid–water. The above mentioned spraying reagent can be used for the identification of aromatic compounds containing a NH_2 group. This spraying reagent not only gives well-defined spots, but is composed of ingredients easily available in the laboratory.

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