Indian Journal of Chemistry
Vol. 26A, April 1987, pp. 360-362

Selective Detection of Picric Acid with Indole by Capillary Solid-state Spot Test

ALI MOHAMMAD* & NAIM FATIMA

Chemistry Section, Z.H. College of Engineering and Technology, Aligarh Muslim University, Aligarh 202001

Received 24 *March* 1986; *revised* 14 *July* 1986; *rerevised and accepted* 23 *September* 1986

Capillary solid-state spot test technique has been applied for the selective detection of picric acid using indole as the reagent. An attempt has been made to make the test specific for picric acid by using a glass wool plug between the reactants.

Rastogi and coworkers developed a capillary technique[1] to study the kinetics of solid state reactions by following the movement of the coloured product boundary formed at the junction in a glass capillary. Qureshi *et al.*[2-4] have extended this technique for the qualitative analysis of organic as well as inorganic compounds and termed it as capillary solid-state spot test technique.

In contrast to the conventional spot test techniques in which the colour formed is the only indication, the new technique offers three variables: (i) the colour at the junction, (ii) the length of the coloured boundary, and (iii) the direction of movement of the coloured boundary. Thus, two substances giving the products of the same colour can not be distinguished by conventional spot tests but they can be distinguished either on the basis of product boundary lengths (if they diffuse with different rates) or on the basis of direction of the product boundary movement (if they move in opposite directions) by using capillary technique. The selectivity of solid-state test can be further improved by allowing the reaction to occur through an air gap between the reactants.

Although nitro compounds are an important class of reagents and form coloured charge-transfer complexes with many substances, no work has been reported on the colour reaction of picric acid with aromatic amines or hydrocarbons for its selective detection in the solid-state. Therefore, it was decided to develop a selective solid-state test for picric acid using indole as a reagent.

2,4-Dinitrotoluene (Fluka), picric acid and indole (BDH, AR) were used after crystallization to constant melting point. All the other reagents were of AR grade and used as such. The powders used were of 50-100 mesh size. Intimate mixtures of variable concentrations of test substances or the reagent were prepared in potassium chloride.

Procedure:

(*i*) *Solid-state detection by trituration*

About 5-10 mg of the powdered test material was rubbed with several mg of indole in the depression of a white spot-plate. The colour developed at room temperature (30°C) was recorded.

(*ii*) *Detection by the capillary solid-state spot tests*

The well-powdered reagent was introduced from one end of a 10 cm capillary (3 mm bore) with the help of two iron rods. The test material was similarly introduced from the other end so that the two materials came in close contact with one another in the middle of the capillary. Care was taken to maintain the packing pressure uniform as far as possible. The capillary was kept at desired temperature for a fixed time interval. The colour at the junction, direction of the movement and the length of the coloured boundary were recorded. No product produced any fluorescence under a UV lamp.

The limits of identification were determined by starting with several synthetic mixtures containing 1-0.01% nitro compounds. The synthetic mixtures were prepared by mixing weighed amounts of nitro compounds with potassium chloride as diluent. The mixtures containing 1-0.01% nitro compounds were triturated in a mortar till they became homogeneous. The tests were conducted as described above at room temperature (30°C) on spot plate and at 40°C in the glass capillary. The sensitivity of the test slightly improved when the capillary of 3 mm bore was replaced by a capillary of 1 mm bore but boresize was not critical.

(*iii*) *Glass wool plug modification for specific test of picric acid*

When a glass wool plug of 4 mm was introduced between the test sample and indole, an orange colour was obtained at the glass wool-test material junction within 30 min only when picric acid was present in the sample. None of the substances mentioned in Table 1 or their mixtures gave any colour at the glass wool test material junction in the absence of picric acid even after 2 h. Therefore, the test is specific for picric acid.

The results obtained for colour reactions of some nitro compounds with indole are given in Table 1. Indole produces yellow to orange coloured products with nitro compounds on trituration as well as in the capillary. Though the proposed method is slower than the wet tests, it is more selective and free from the complicating effect of the solvent. Table 1 indicates

Table 1 — Solid-state Colour Reactions of Indole with Some Nitro Compounds under Different Experimental Conditions

Compounds	Trituration solid-state spot test reactions (30°C)	Capillary solid-state spot test reactions			
		With pure indole			With 1% indole
		30°C 30 min CB/l,DM	30°C 1 h CB/l,DM	45°C 1 h CB/l,DM	30°C 1 h CB/l,DM
p-NT	Y(m)	—	—	—	Y/NM
DNT	O-R	O/3.0, TM	O/4.0, TM	O/10.0, TM	Y/NM
PA	O	O/1.0,TM	O/1.5,TM	O/2.0,TM	O/1.5,TR
o-DNB	Y	O/NM	O/NM	O/NM	NC
m-DNB	O-R	Y/1.0,TM	Y/1.5,TM	Y/2.0,TM	Y/NM
CDNB	O-R	Y/NM	Y/NM	O/2.0,TM	Y/NM
o-NA	R-Br	—	—	—	—
m-NA	NCC	NC	—	—	—
p-NA	NCC	NC	—	—	—
m-NP	Y	Y/NM	Y/NM	Y/2.0,TM	NC
m-NBA	Y	NC	NC	Y/1.0,TM	NC
p-NBA	Y	Y/NM	Y/NM	Y/NM	Y/NM

p-NT = *p*-nitrotoluene; DNT = 2,4-dinitrotoluene; PA = picric acid; DNB = dinitrobenzene; CDNB = 1-chloro-2,4-dinitrobenzene; NA = nitroaniline; NP = nitrophenol; NBA = nitrobenzoic acid; CB = colour of product boundary; DM = direction of movement of coloured boundary; l = length of coloured boundary in mm; TR = towards reagent; TM = towards test material; NC = no colour; NCC = no change in colour; NM = no movement; m = melted; Y = yellow; O = orange; R = red; Br = brown.

that thickness of the coloured boundary increases with time and temperature. The direction of movement and the thickness of the coloured boundary depend upon the concentration of the reagent. With pure indole, the product boundary in all the cases moves towards test material showing that indole is the only diffusing species. When the reagent concentration is reduced to 10% or 1%, none of the nitro-compounds shows any movement of coloured boundary upto 1 h except picric acid. It produces an orange product with 10% indole which moves in both the directions showing counter diffusion of the reactants while with 1% indole only picric acid is diffused to give a boundary length of 1.5 mm toward reagent. Thus, picric acid can be selectively detected using lower concentration of indole.

None of the nitro compounds listed in Table 1 except picric acid gave any colour at glass wool-reagent or test material junction when the capillaries with a glass wool plug in between the reagent and the nitro compounds were kept at 40°C for 2 h. An orange colour formation at glass wool-picric acid junction within 30 min made the test specific for picric acid. The presence of 10% picric acid in the sample containing 90% of other nitro compounds was successfully detected by keeping the capillary at 40°C for 30 min and observing the orange colour at the glass wool-test material junction. The higher reactivity of picric acid with indole vapours is probably due to the presence of three nitro groups in its molecule.

A novel feature of capillary solid-state spot tests is that the product formed at the junction can clearly be distinguished by the separated boundaries. Therefore, the non-reacting coloured ions do not interfere in the test and the test materials forming coloured products which differ subtly from those of their own or reagent colour can be detected satisfactorily by this technique. Such a detection is not possible in the solution state or even by powder trituration method. Thus, the presence of 10% picric acid, *m*-dinitrobenzene and 2,4-dinitrotoluene (DNT) was successfully detected in the mixture containing 90% Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$ and diphenylcarbazide by observing orange ring at the interface of the reactants in the capillary at 48°C within 30 min. These ions do not give any colour with indole in the absence of nitro compounds in capillary.

No colour was observed when indole was triturated with barbituric acid, barbitone, thiourea, allyl thiourea, phenylurea, orcinol, resorcinol, hydroquinone, maltose, xylose, sarcosine, acridine, nicotinic acid, sulphosalicylic acid, phenyl carbazide, semicarbazide hydrochloride and diphenyl carbazide.

The limits of identification for nitro compounds by powder trituration and by capillary solid state test were found to be in the range of 0.01-1.0%. A detailed study of the reaction between indole and DNT is under progress. The kinetic, thermodynamic and spectral

studies of this reaction in the solid state show the formation of a weak charge-transfer complex similar to that formed by DNT with diphenylamine[5]. Similar products are expected for other nitro compounds.

One of the authors (A.M.) wishes to thank the UGC, New Delhi for providing financial assistance.

References

1 Rastogi R P, Bassi P S & Chadha S L, *J phys Chem*, **66** (1962) 2707.
2 Qureshi M, Rathore H S & Mohammad A, *Talanta*, **23** (1976) 874.
3 Qureshi M, Mohammad A & Raju G G, *Talanta*, **28** (1981) 817.
4 Qureshi M, Rathore H S, Mohammad A & Akhtar M N, *Ann Chimica*, **69** (1979) 231.
5 Qureshi M, Nabi S A, Mohammad A & Qureshi P M, *J Solid State Chem*, **44** (1982) 186.