Solid State Reactions of 2,4-Dinitrotoluene. Detection and Semiquantitative Determination of Indole, Diphenylamine, and *p*-Dimethylaminobenzaldehyde

Syed Ashfaq NABI, Ali MOHAMMAD, and Pushkin Mohammad QURESHI*

Department of Chemistry, Aligarh Muslim University, Aligarh-202001, India

(Received May 24, 1982)

Synopsis. Solid state colour reactions of 2,4-dinitrotoluene have been used for the selective detection of organic compounds and semiquantitative determination of indole, *p*-dimethylaminobenzaldehyde and diphenylamine in a glass capillary. Phloroglucinol and tryptophan do not interfere with the determination of indole. A glass wool plug modification makes the selective test almost specific for indole.

2,4-Dinitrotoluene (DNT) gives interesting colours with a number of compounds.[1-5] A recent study has proposed the use of DNT for the detection of amines.[6] In this note we present methods for the solid state detection and semiquantitative determination of some organic compounds.

Reagents. DNT (Fluka) and *p*-dimethylaminobenzaldehyde (*p*-DAB) (E. Merck) were used. All other reagents were reagent grade and used without further purification. Apparatus: VSU-2(GDR) reflectance spectrophotometer and Perkin Elmer 621 spectrometer were used for obtaining UV-visible reflectance and IR transmission spectra respectively.

Procedure

Solid State Detection. About 5—10 mg of the solid (or 5—10 μl for liquids) was rubbed with several mg of powdered DNT in the depression of a white spot plate. This was to check the colours in neutral medium. To see the effect of acidic or basic medium sodium carbonate or oxalic acid was added to the test substance and DNT; the content was again rubbed and the colour observed was then noted.

Detection by the Capillary Solid State Tests. The well powdered reagent was introduced from one end of a 10 cm capillary (3 mm bore) with the help of an iron rod. The test material was introduced similarly from another end till the two materials came in close contact with one another. Both the ends of the capillary were closed with the help of two cotton plugs. The capillary was kept in an oven at 42±2 °C for one hour. This temperature was chosen as some of the solids used in this study melted at 45 °C. The colour of the product formed at the junction was recorded. No product gave any fluorescence under a UV lamp.

The limits of identification of indole, *p*-DAB, and diphenylamine (DPA) were determined by mixing weighed amounts of well powdered sodium carbonate as a diluent. The mixture was triturated in a small mortar till it became homogeneous. Such a mixture is termed as a synthetic mixture in this paper. The synthetic mixtures contained 1—10% of the test substance. Tests were conducted in the capillary as described above. The synthetic mixture containing the largest percentage of the test substance was tried first and the colour at the junction noted. The procedure was repeated with synthetic mixtures containing lower percentages of the test material till no colour was produced at the junction. In this way the limit of identification was determined for each test substance.

Semiquantitative Determination by Capillary Solid State Tests. Approximately 400 mg of the reagent was introduced from one end of the capillary. Synthetic mixtures containing 10—100% of the test material were then introduced as described above. Three types of synthetic mixtures were tried *i.e.* those diluted with sodium carbonate oxalic acid and starch. The set of capillaries containing different percentages of indole or DPA were heated in an oven at 45± 2 °C for 1 h. This temperature was chosen as indole melts at 52 °C and DPA at 54 °C. As *p*-DAB melts at 75 °C the capillaries containing *p*-DAB were allowed to react at 65 °C for 1 h. The length of the coloured boundary formed at the junction was proportional to the concentration of the test material.

Semiquantitative Determination of Indole in the Presence of Tryptophan and Phloroglucinol. For the semiquantitative determination of indole in phloroglucinol or tryptophan mixtures, various synthetic mixtures of indole were prepared using phloroglucinol or tryptophan as diluents. These two substances were chosen as they generally interfere in the tests of indole.[7] The capillaries containing the reagent and the synthetic mixture were kept at 45±2 °C for 1 h. Capillaries were filled with synthetic mixtures containing 10—100% of indole. The same slope was obtained when a calibration curve for indole was prepared by using potassium chloride or sodium carbonate as a diluent instead of phloroglucinol or tryptophan (Fig. 1). This implies that the latter two compounds do not interfere with the determination of indole. The starch plot does not pass through the origin, hence starch should not be used as a diluent. Similar studies show that DPA can be determined in the presence of *N,N'*-diphenylthiourea and tryptophan.

Glass Wool Plug Modification for Selective Determination of Indole. When a glass wool plug was introduced between DNT and the test samples, a yellow colour was obtained at the DNT-glass wool boundary only in the case of indole. None of the substances in Table 1 and their mix-

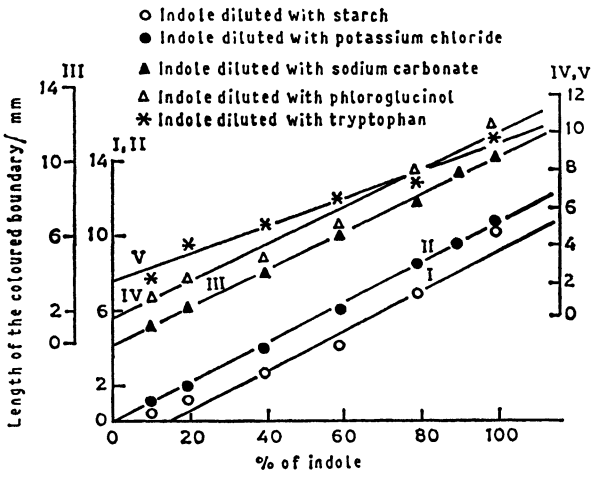

Fig. 1. Semiquantitative determination of indole, in the presence of different diluents.

Table 1. Colour reactions of organic compounds with DNT

No.	Compound	Amount taken/mg	Temperature of the spot test/°C	Colour of the spot test[a)]	Thickness of the coloured boundary/mm at 42±2 °C
1	DPA	100	25	OR	10.0
2	Benzidine	100	35	BR	0.5
3	2-Naphthylamine	100	35	Y	—
4	*p*-Toluidine	100	35	O	16.0
5	*N*-Phenyl-2-naphthylamine	100	35	Y	1.5
6	*o*-Phenylenediamine	100	35	B	1.0
7	*p*-Phenylenediamine	100	35	B	0.0
8	*o*-Nitroaniline	100	35	Y	2.0
9	*m*-Nitroaniline	100	35	Y	TR[b)]
10	*p*-Nitroaniline	100	35	Y	—
11	*p*-DAB	100	35	O	2.5
12	*p*-Dimethylaminocinnamaldehyde (*p*-DAC)	100	35	Y	TR[b)]
13	1-Naphthol	100	35	Y	TR[b)]
14	2-Naphthol	100	35	Y	TR[b)]
15	*o*-Nitrophenol	100	35	Y	12.5
16	*m*-Nitrophenol	100	35	Y	—
17	*p*-Nitrophenol	100	35	Y	2.5
18	2,4-Dinitrophenol	100	35	Y	—
19	Indole	100	35	Y	10.5
20	Brucine(anhydrous)	100	35	Y	TR[b)]
21	8-Quinolinol	100	35	Y	—
22	Phenol	100	35	Y	—
23	Ethylenediamine (liquid)	100	35	Bl	—
24	1,3-Propanediamine (liquid)	100	100	Bl	—

a) Y: Yellow, B: Brown, BR: Brick red, O: Orange, Bl: Blue, OR: Orange red.
b) TR: Thin ring.

tures gave any colour. The test is therefore specific for indole.

Results and Discussion

The colours obtained by direct trituration of test material with DNT are given in Table 1.

The colour reactions with DNT were not altered when performed in the presence of oxalic acid or sodium carbonate. The colour reactions of DNT were studied with representative members of aliphatic amines, phenols, substituted phenols, ketones, aldehydes, ureas, sugars, amino acids, acids, alcohols, hydrocarbons, and their derivatives, and ethers. No substance except those reported in Table 1 gave any colour.

As benzidine gives a characteristic colour with DNT it was detected by triturating with DNT at 35 °C in the presence of phloroglucinol, tryptophan, *p*-DAB, brucine, DPA, *p*-chlorobenzaldehyde, *o*- or *m*-nitroaniline, 2-hydroxy-3-methylbenzaldehyde, maltose, glucose, phenylthiourea, citric acid, nicotinic acid, and *p*-toluidine.

The limits of identification for indole, *p*-DAB and DPA by the capillary solid state test are 7.7, 2.3, and 1.9 μg respectively. The limit of identification for indole when a glass wool gap of 4 mm was introduced between the reagent and indole is 155 μg. Each point in Fig. 1 is an average of five readings with precision and accuracy of 3—4%.

Of the 138 compounds studied, only aromatic amines, phenols, naphthols, indole, *p*-DAC, brucine, and 8-quinolinol gave coloured reactions with DNT.

The UV, visible, and IR spectra of the compounds formed by mixing DNT with DPA, *p*-DAB, or indole

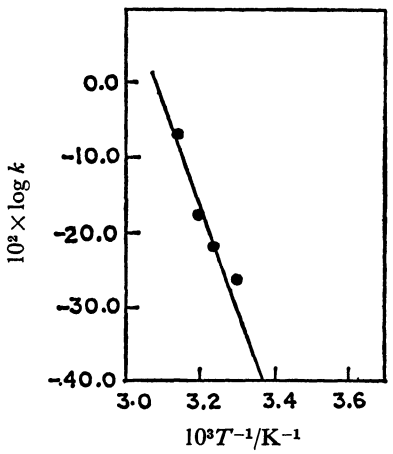

Fig. 2. Dependence of reaction rate on temperature for the DNT–DPA solid-state reaction, whereby:
$$\xi = k \log t,$$
where t is time in h, and ξ is length of coloured boundary.

are in consonance with the formation of weak charge transfer complexes.[8-14]

The coloured boundary was found to increase with time and temperature. Thus a plot of $\log k$ *vs.* $1/T$ obtained for the DNT–DPA reaction is given in Fig. 2. The plot was used in another connection that is to obtain the energy of activation of the DNT–DPA solid-state reaction.[15] Similar plots are expected for the DNT–*p*-DAB and DNT–indole reactions.

The authors thank Prof. W. Rahman for research facilities. The C. S. I. R. (India) is thanked for financial assistance.

References

1) T. Sinomiya, *Bull. Chem. Soc. Jpn.*, **15**, 259 (1940).
2) S. J. Stephenes, G. E. Hargis, and J. B. Entrikin, *Proc. Louisiana Acad. Sci.*, **10**, 210 (1948).
3) T. Canback, *Farm. Revy.*, **48**, 217, 234, 849 (1949).
4) H. E. Malone, *Talanta*, **22**, 97 (1975).
5) F. Feigl, "Spot-tests in Organic Analysis," 7th ed, Elsevier, New York (1966).
6) S. A. Nabi, A. Mohammad, and P. M. Qureshi, *Talanta*, **26**, 1179 (1979).
7) V. Anger and S. Ofri, *Microchim. Acta*, **1964**, 772.
8) R. E. Gibson and H. Loeffler, *J. Am. Chem. Soc.*, **62**, 1324 (1940).
9) W. R. Burton and R. E. Richards, *J. Chem. Soc.*, **1950**, 1316.
10) H. Kainer and W. Otting, *Chem. Ber.*, **88**, 1921 (1955).
11) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin (1961), pp. 94, 103.
12) L. J. Andrews and R. M. Keefer, "Molecular complexes in organic chemistry," Holden-Day, San Francisco (1964), p. 32.
13) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).
14) Y. Matsunaga, *Nature*, **205**, 72 (1965).
15) M. Qureshi, S. A. Nabi, A. Mohammad, and P. M. Qureshi, *J. Solid. State. Chem.*, (in press).