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Note

A method for the detection of nitrate esters

T. URBAŃSKI
Chemical Faculty, Technical University (Politechnika), 00-662, Warsaw (Poland) and National Chemical Laboratory, Poona-8 (India)
and
T. KRASIEJKO
Institute of Organic Industry, Warsaw-Żerań (Poland)
and
W. POŁUDNIKIEWICZ
Faculty of Pharmacy, Warsaw Medical School, Warsaw (Poland)

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It has been found[1–4] that organic nitric acid esters in an anhydrous non-polar solvent oxidize tetramethyl-*p*-phenylenediamine (TMPD) to yield the so-called Wurster cation[5], which is coloured intensely violet-blue. Nitric acid esters with five or six nitro groups in anhydrous, non-polar solvents produce further reactions, including the formation of brown-coloured charge-transfer complexes[1,2,4]. Nitric acid esters that contain a smaller number of nitro groups (one to four) give a stable violet-blue colour[4], the Wurster cation being unchanged for at least 24 h at room temperature.

These characteristics offer the possibility of using TMPD as a reagent for the detection of nitric acid esters in general and, for substances with a smaller number of nitro groups, of using the reaction in thin-layer or paper chromatography.

We therefore examined some esters of nitric acid, *viz.*, glycerol trinitrate (nitroglycerine; NG), diglycerol tetranitrate (DGTN), ethylene glycol dinitrate (EGDN), 1,2-propylene glycol dinitrate (PGDN) and trimethylene glycol dinitrate (1,3-propylene glycol dinitrate; TMGD).

EXPERIMENTAL AND RESULTS

Glass plates were covered with a 0.25 mm thick layer of neutral aluminium oxide (M. Woelm, Eschwege, G. F. R.). The layers were activated by heating the plates at 110° for 1 h.

The nitrate esters were dissolved in acetone (20% solutions), and TMPD was used as a 0.5% solution in acetone. The other solvents (chloroform and toluene) were of analytical-reagent grade.

The following procedure was used in order to obtain standard chromatograms. A 10-μg amount of nitric acid esters in solution were placed on the starting line of the plate, and the solution was developed in a chamber with the mobile phase, consisting of chloroform–toluene (85:15), until a height of 15 cm was reached.

The plate was dried and then covered with the TMPD solution. After a few minutes, violet-blue spots appeared, the formation of which could be accelerated by briefly irradiating them with an UV lamp.

In order to establish the sensitivity of the method, a few spots were placed on the plate, corresponding to amounts from 0.01 to 0.1 μg of NG. It was established that the smallest detectable amount of NG was 0.02 μg. Diglycerol tetranitrate was detectable in an amount of 0.05 μg and the other three nitrate esters (EGDN, PGDN and TMGD) were detectable in amounts of 0.1 μg.

The strongest blue spot on a layer of aluminium oxide was given by NG, less intense was the colour given by DGTN and even weaker were the spots given by glycol dinitrates. The higher intensity produced by NG compared with that produced by glycol dinitrates is evidently due to the higher enthalpy of formation of the Wurster cation by NG compared with the enthalpy with EGDN, all nitrate esters being electron acceptors[4].

It is well known that nitrate esters are often used in mixtures with aromatic nitro compounds. Some of the dinitro- and most of the trinitro-compounds also give colour reactions with TMPD. However, *m*-dinitrobenzene and dinitrotoluenes give a yellow or beige colour, different from that given by nitrate esters. *sym*.-Trinitrobenzene and some trinitrotoluenes produce darker spots, which differ appreciably in their R_F values from those produced by nitric acid esters.

A detailed description of the chromatography of aromatic nitric acid esters with TMPD will be published elsewhere.

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