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On a New Colour Reaction of Nitromethane and Some Aromatic Nitrocompounds

by

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It is known that most aromatic polynitro compounds give intensely coloured products with a number of compounds possessing an active methylene group in alkaline medium in organic solvents.

One such reaction is known as the Janovsky reaction [1], [2] and was studied by a number of authors [3]—[7].

The reaction of aromatic polynitrocompounds with primary nitroparaffins in alkaline medium in alcoholic solution was now examined. It was now found that the most typical colour reaction can be obtained by *m*-dinitrobenzene and nitromethane. *m*-Dinitrobenzene gives a very faint colour with a maximum at 480 mμ under action of sodium hydroxide in alcoholic solution, but addition of nitromethane produces a crimson colour. Spectroscopic investigation shows a strong band at 460 mμ and a shoulder at 540 mμ.

The other primary nitroparaffins, such as nitroethane, 1-nitropropane etc. give a conspicuous crimson colour with *m*-dinitrobenzene when they are present in larger quantity only, and the concentration is *c* 300 times higher than that of nitromethane. The colour reaction of primary nitroparaffins with *m*-dinitrobenzene has therefore a selective character and can be used to determine nitromethane in presence of other primary nitroparaffins.

So far only one such selective reaction was described, namely that of nitromethane with sodium 1,2-naphthaquinone-4-sulphate suggested by Turba, Haul and Uhlen [8] and studied in detail by L. R. Jones and Riddick [9].

Trinitrocompounds, such as sym-trinitrobenzene and α-trinitrotoluene give also a colour reaction with primary nitroparaffins in presence of alkali in alcoholic medium, and the intensity of the colour is much higher than in the instance of *m*-dinitrobenzene.

The reaction with trinitrocompounds could probably be used as a colour reaction of primary nitrocompounds. However, the use of the trinitrocompounds is not advisable. The latter give an intense colour with alcoholic sodium or potassium hydroxide without nitroparaffins and the presence of nitroparaffins only changes the shade. Thus, sym-trinitrobenzene shows two maxima with alcoholic NaOH: 430 and 470 mμ. In presence of nitromethane or 1-nitropropane or 1-nitrohexane they are subjected to bathochromic shifting to 450 and 540 mμ respectively.

α-Trinitrotoluene gives one maximum at 520 mμ with alcoholic NaOH. In presence of nitromethane the maximum is 455 mμ.

The change of the colour of trinitrocompounds under the action of a primary nitroparaffin is therefore not sufficiently typical.

Procedure

Reagents. 2% solution of sodium hydroxide (analytical grade) in anhydrous or 95% ethanol.

0.1% solution of *m*-dinitrobenzene (m.p. 90°C) in anhydrous or 95% ethanol.

Determination. A few (e.g. 5) drops of sodium hydroxide solution are added to 2 c.c. of the solution of *m*-dinitrobenzene.

A few c.c. (e.g. 2) of the investigated alcoholic solution containing nitromethane are added to the above solution. The colour thus developed is compared with that of the blank sample composed of *m*-dinitrobenzene and sodium hydroxide solution — only. The colour of the "blind" sample is very faint.

Sensitivity. The limit of the sensitivity of the test is 0.05% of nitromethane in the investigated alcoholic solution. A concentration below this limit does not give appreciable change of colour.

The sensitivity of the test is reduced by the presence of organic solvents such as ether. Small quantity of water (e.g. 5%) does not reduce the sensitivity of the test, but larger concentration of water lowers it.

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