ACTION OF SULPHURIC ACID ON TETRYL IN THE COLD AND FORMATION OF METHYL PICRAMIDE*

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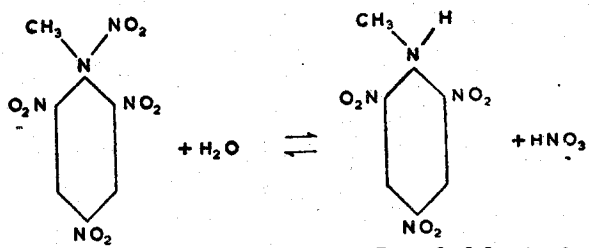
ABSTRACT

Evidence has been obtained to show that the dissolution of tetryl in sulphuric acid in the cold results in reversible hydrolysis, the tetryl remaining in equilibrium with the products of reaction, amongst which methyl picramide is one. The reaction has been made to proceed in either direction by adjusting the concentration of nitric acid. Methyl picramide has been isoalted and its properties studied.

Mitra and Srinivasan[1] reported that one mol. of tetryl (N-nitro-N-methyl-2 : 4 : 6-trinitro-aniline) dissolved in cold conc. sulphuric acid liberated one mol. of nitric acid. The nitrogen so split off appears to be the nitramine nitrogen. The nature of the product remaining in solution in sulphuric acid, however, required elucidation.

Mertens[2] found that on heating with various solvents, tetryl gives nitric acid and N-methyl-2 : 4 : 6-trinitro-aniline (otherwise described as methyl picramide). Davis and Allen[3] observed that tetryl is unaffected by hot dilute sulphuric acid but dissolves in conc. sulphuric acid at 100°C with the formation of a red solution from which tetryl can be precipitated by pouring into cracked ice. 35 gm. tetryl + 100 c.c. conc. sulphuric acid kept at room temperature for 15 days and thereafter poured into ice produced a gummy mass. They recovered 20 per cent methyl picramide (m.p. 111·8°C) from the gummy product so obtained. These authors tentatively suggested that the reaction was the reverse of the familiar one in which methyl picramide was converted to tetryl.

In the present study, evidence has been obtained to show that the dissolution of tetryl in sulphuric acid in the cold results in reversible hydrolysis, the tetryl remaining in equilibrium with the products of reaction:



N-nitro-N-methyl-2 : 4 : 6-trinitroaniline

N-methyl-2 : 4 : 6-trinitroaniline

The reaction has been made to proceed in either direction by adjusting the concentration of nitric acid.

* Represents work done during World War II.

We used a large excess of sulphuric acid to effect the solution of tetryl in the acid in a few hours at temperature near about 0°C. This low temperature was primarily chosen for the reason that our object was to study the tetryl-sulphuric acid reaction under the conditions found most suitable for the estimation of tetryl. The use of such a low temperature obviated most of the side reactions as evidenced by the little or no formation of resinous products, and a fairly good yield of methyl picramide (about 70 per cent of the theoretical) was obtained in a single crystallisation from benzene. If the temperature was not maintained at about 0°C during dissolution and precipitation, a gummy mass containing little methyl-picramide was invariably formed. This method was thus a distinct improvement over the method reported by Davis and Allen[3] who got only a 20 per cent yield of methyl picramide after prolonged reaction (15 days) at the room temperature. Although working with smaller quantities of tetryl, greater yields of methyl-picramide could be obtained, some quantity of tetryl was invariably found to remain in all cases mostly in the diluted acid layer, showing that the reaction does not proceed to completion by mere dilution with water.

The removal of nitric acid by ferrous ammonium sulphate could not be used to isolate methyl picramide, since the ferrous salt itself formed a complex with the methyl picramide. This complex was fairly resistant to acid treatment and appeared to decompose only by boiling with strong alkali.

The literature gives the melting point of methyl picramide as 110°—111°C (Beilstein[4]); 111·8°C (Davis and Allen[3]); 110·4°—110·8°C (Gardner and Abernethy[5]); 114·8°C (James *et al*[6]). We found that the first crystallisation of the crude product from acetone-alcohol melted at 110°—111°C, and subsequent recrystallisation from benzene gave pure methyl picramide, m.p. 114·2°—114·4°C.

The crystalline structure of methyl picramide (Fig. 1, Microphotograph) as obtained by us differed from the needle shape attributed to it by Beilstein[4] and James *et al*[6].

FIG. 1—Microphotograph.

In addition to melting point, tests carried out for the identification of methyl picramide were: (*i*) estimation of nitro-nitrogen ($TiCl_3$ method), (*ii*) preparation of the nitroso derivative, (*iii*) conversion to tetryl and (*iv*) absence of nitric acid on dissolution in sulphuric acid (*i.e.*, freedom from tetryl).

The approximate purity of methyl picramide, tetryl and of their mixtures in the different fractions, at various stages of purification was adjusted from their rough melting points (methyl picramide fraction 108—114°; tetryl fraction 127—129°C. The brown ring test for nitric acid (released from tetryl by conc. sulphuric acid) formed an additional test for tetryl in the different fractions.

Experimental

Preparation of Methyl Picramide

Powdered tetryl from 5—10 gm. was treated with conc. sulphuric acid (180 c.c. per gm. of tetryl). The dissolution was effected at ice cold temperature and took 6 to 8 hrs. to complete. The cold solution (straw-yellow in colour) was poured in a thin stream into a large quantity (10 lbs.) of crushed ice under vigorous stirring. An orange-yellow precipitate (fraction A) settled down below the supernatant yellow solution (fraction B). With a few lumps of ice still floating, the precipitate was filtered at the pump and washed twice with ice water.

Fraction A—Orange-yellow precipitate—This was dissolved in a minimum quantity of acetone, and alcohol added till the solution became just turbid. After standing overnight fine crystals separated. These were collected by filtration. The filtrate on further concentration and standing, gave more crystals which were added to the first crop. The yield of methyl picramide from 10 gm. of tetryl was about 70 per cent.

The methyl picramide thus obtained was crystalline in structure, melting at 108—110°C. The product, on recrystallisation from benzene, gave yellow, shining crystals with a melting point of 114·2°—114·4°C. The amount of nitro-nitrogen, estimated by $TiCl_3$ method was 17·27 per cent (theoretical 17·35%).

Fraction B—Yellow aqueous filtrate—On shaking this up with benzene in a separator, the aqueous layer became colourless, the benzene layer taking up all the yellow colour. The extracted aqueous layer was discarded. On evaporating off the solvent from the benzene extract, an oily substance separated which had an offensive penetrating odour and solidified to an amorphous mass on standing, softening between 75°—96°C. and indicated the presence of large quantities of tetryl (nitric acid test). On further purification, the bulk of the product was found to be tetryl (about 15 per cent of the original).

Fraction C—Mother liquor from Fraction A—Concentration to a smaller bulk gave an amorphous semi-solid, softening below 90°C; it contained tetryl (nitric acid test). A few fractional crystallisations were not of much help; the material was not examined further.

There was no evidence of picric acid in any of the fractions.

Reversibility of the reaction with sulphuric acid

(*a*) About 0·5 gm. powdered tetryl was dissolved in cold conc. sulphuric acid (about 100 c.c.), and to the solution 20 c.c. conc. nitric acid (sp. gr. about 1·4) added. On diluting the mixed solution with water, yellow crystals of pure tetryl were precipitated, m.p. 128°-129°C.

(*b*) About 0·5 gm. powdered tetryl was treated with a mixture of 20 c.c. conc. nitric acid and 20 c.c. conc. sulphuric acid and heated on a water bath under reflux for 30 min. There was no browning, unlike as when tetryl is heated with conc. sulphuric acid only. On diluting the solution pure tetryl was precipitated.

(*c*) 0·5 gm. methyl picramide was warmed with a 20 c.c. mixture of sulphuric acid and nitric acid (1 : 3) on a water bath till it dissolved completely. On dilution with water tetryl was precipitated. Yield about 95 per cent of theoretical.

Properties of Methyl Picramide

Yellow shining crystals melting at 114·2°—114·4°C; very slightly soluble in hot water; dissolves in acetone, benzene, and nitrobenzene; soluble in hot acetic acid, hot alcohol and cold conc. sulphuric acid, sparingly soluble in carbon tetrachloride, chloroform and petroleum ether.

On nitration, the material gives tetryl; does not give any brown ring test with conc. sulphuric acid and ferrous sulphate; gives a nitroso derivative.

Preparation of Nitroso Derivative

Nitrous fumes were passed through a warm solution of methyl picramide in glacial acetic acid till the solution became green. On diluting with a small quantity of water, pale yellow crystals of nitroso methyl picramide separated with a m.p. of 106°—107°C (decomp.). Beilstein [4] gives the m.p. as 106·5°C.

References

1 Mitra and Srinivasan, Analyst, *70*, 418 (1945)

2 Mertens, Ber., *19*, 2123 (1886).

3 Davis and Allen, J. Amer. Chem. Soc., *46*, 1063 (1924).

4 Beilstein, Handbuch der Organichen Chemie, 4th Edn., *12*, 764.

5 Gardner and Abernethy, Proc. Roy. Soc., *99A*, 213 (1921).

6 James, Jones and Lewis, J. Chem. Soc., *117*, 1273 (1920).