Defence Science Journal, Vol. 4, No.2, April 1954, pp. 67-73

PHOTO DECOMPOSITION OF AROMATIC NITROCOMPOUNDS*

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ABSTRACT

When aqueous solutions/suspensions of mononitro aromatic compounds are exposed to sunlight, nitrous acid and the corresponding phenol are produced. The nitrocompounds also give rise to nitrosophenols which further react to form azoxy compounds. In case of a polynitrocompound like T. N. T. a complex polymeric photodecomposition product is obtained as a result of more than one reaction taking place simultaneously.

The photochemical reactions of aromatic nitrocompounds have been studied by many workers, [1, 2, 3]. The nitro group is generally found to oxidise other organic bodies present, while it is itself reduced to nitroso, azo and azoxy derivatives according to the Bamberger reaction.[4] Oxidation of side chains on the same molecule by a nitro group is a special case of this photoreaction. [5, 6, 7].

The photodecomposition of 2 : 4 : 6 trinitrotoluene has been studied by many workers. [8], [9] Krauz and Turek[10] claimed to have isolated picric acid and trinitrobenzoic acid from the photodecomposition product of T. N. T. Lodati[11] observed that in diffused light, T. N. T. liberated nitrous vapours in three months. Schultz & Ganguly[12] examined a water extract of T. N. T. exposed to sunlight and stated that by the action of sunlight, T. N. T. is converted to two tautomeric quinoneoximes, $C_7H_5O_6N_3$, of melting points above 280°. These were considered to be formed by the oxidation of the methyl group by the two ortho nitro groups which were reduced to nitroso groups.

Mitra and Srinivasan[13] have studied the photo decomposition of T. N. T. and have observed that

(*a*) the quantity of photodecomposition product formed depends upon the duration of the exposure to sunlight,

(*b*) the decomposition takes place with greater facility in dissociating solvents and not at all in nondissociating solvents. Presumably a transformation of the T. N. T. to its acid form takes place prior to decomposition, and

(*c*) the photodecomposition product bears a strong resemblance to the product obtained by the action of alkali on T. N. T.

Mitra and Srinivasan[13] have not suggested any probable structure for the photodecomposition product of T. N. T. The present work was undertaken with a view to elucidating further the nature of the photodecomposition of aromatic nitrocompounds in general.

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* From a thesis submitted by the author in July 1949 to the University of Bombay for the Ph. D. Degree.

The photodecomposition product obtained by exposing solid 2 : 4 : 6 trinitrotoluene to sunlight was found to be a resinous material, having a molecular weight (ebullioscopic, solvent acetone) 5 to 6 times that of T. N.T. and a lower nitrogen content. The evolution of nitrous fumes after exposure to sunlight was confirmed. When T. N. T. was exposed to sunlight, in the form of an aqueous suspension, the amount of nitrous acid liberated after exposure to sunlight, was found to depend on the pH of the suspension and was negligible at pH 3 and below. The nitrous acid was estimated colorimetrically using the Griess-Ilosvay reagent.

The photodecomposition product of T. N. T. was of an intractable nature and no identifiable products could be obtained by its oxidation or reduction using a variety of reagents. The absorption spectrum in the visual region of the photodecomposition product and alkali decomposition product of T. N. T. were found to be very similar.

The photodecomposition of some simple nitro compounds was then studied. Aqueous suspensions of Nitrobenzene, paranitrotoluene and 1-nitronaphthalene, when exposed to sunlight were found to give phenol, p-cresol and 1-naphthol (with a trace of 2-naphthol) respectively, along with nitrous acid. This shows that the overall reaction is

$$RNO_2 + H_2O \longrightarrow R\ OH + HNO_2$$

This reaction has not been reported by previous workers. The amount of nitrous acid liberated in these cases also was found to depend on the pH of the suspensions. It was confirmed that the suspensions even at high pH values and high temperatures (95°C) did not liberate nitrous acid, if they were kept in dark.

The photodecomposition of 1-nitronaphthalene was further studied in detail. Apart from the formation of 1-naphthol (with a trace of 2-naphthol) and nitrous acid mentioned above, 2-nitroso-1-naphthol and 4-nitroso-1-naphthol were separated and identified in the decomposition product. The residual decomposition product consisted of a reddish brown material of indefinite melting point and is probably a complex azoxy compound formed from the above nitrosonaphthols.

During the processing of the photodecomposition product of 1-nitronaphthalene, care was taken so that free nitrous acid was not liberated at any stage, to prevent its reaction with 1-naphthol which was present. The isolation of 2-nitroso-1-naphthol and 4-nitroso-1-naphthol under these conditions indicated that these were formed directly by the photodecomposition of 1-nitronaphthalene.

The formation of 2-nitroso-1-naphthol was rather unusual. In order to eliminate the possibility of its formation from 2-nitronaphthalene which might have been present as an impurity in the 1-nitronaphthalene used, 1-nitronaphthalene was prepared indirectly from purified 1 : 5 dinitronaphthalene by removal of one nitro group through diazotization. The pure 1-nitronaphthalene thus obtained also gave 2-nitroso-1-naphthol on exposure to sunlight. In the formation of 2-nitroso-1-naphthol (and also probably of 4-nitroso-1-naphthol) from 1-nitronaphthalene, a migration of the nitrogen atom therefore appears to be taking place. Incidentally, the melting point of pure 1-nitronaphthalene has been observed to be 56·5° (Corr.) whereas melting points ranging from 56 to 61·5° have been reported in literature.[14, 15, 16, 17, 18.]

In the case of 2 : 4 : 6 Trinitrotoluene all the three nitro groups may undergo either of the above two types of reactions simultaneously. The replacement of one nitro group by a hydroxy group may give rise to two isomeric dinitrocresols. A large number of nitroso-nitro-cresols can also be formed analogous to the formation of nitrosonaphthols from nitronaphthalene, and these may further condense to a complex mixture of azoxy compounds. The methyl group is also likely to condense with a nitroso group, producing benzal-anilino derivatives. It is not, therefore, surprising that a very complex photodecomposition product is finally obtained. Examination of photodecomposition products of T.N.T. after short exposures, is likely to clarify the early stages of the reaction and this work is in hand.

In order to determine, if possible, the effect of substituents on the photodecomposition of a nitro group, the extent of photodecomposition of a number of nitrocompounds was measured in terms of nitrous acid produced after three hours exposure. The neutral nitrocompounds were exposed in the form of their saturated solutions in a buffer solution (pH 7, Borate/Boric acid). The acidic nitrocompounds were exposed in the form of millimolar solutions of their sodium salts in the same buffer solution. The rates of decomposition were found to increase in the following order :—

Xylene musk, p-chloronitrobenzene, 2 : 4 : 6 Trinitrobenzoic acid, 1 : 3 dinitrobenzene, Trinitrobenzene, 2 : 4 dinitrotoluene, m-nitrotoluene, trinitrostilbene, 1-nitronaphthalene, p-nitrophenol, p-nitrotoluene, 2 : 6 Dinitrotoluene, 2-nitronaphthalene, 0-nitrotoluene, 0-nitrobenzyl-alcohol, Nitrobenzene, nitromesitylene, 2 : 4 : 6 trinitrotoluene.

Although no rigorous gradation of the effect of various groups on the rate of photodecomposition of a nitro group is possible, the following qualitative observations can be made :—

(*a*) A substituent group lowers the rate of decomposition, the lowering is more with acidic substituent groups. The reduction in rate of decomposition is more when a substituent is in the meta position and is least when it is in the ortho position.

(*b*) A methyl group increases the rate of decomposition in a polynitrocompound. The case of xylene musk however appears to be a peculiar exception.

EXPERIMENTAL

Experiment I

Photodecomposition product of 2 : 4 : 6 T. N. T.

100 gms of 2 : 4 : 6 T.N.T. (120 B.S.S.) were spread out in a thin layer in an enamelled tray. The tray was covered with a cellophane sheet and exposed to sunlight. The T.N.T. was turned over every day. After one month's exposure (In March at Kirkee, sun temperature Maximum 151°F, Minimum 134°F) the material became dark brown and was soft and sticky at the sun temperature.

The material was repeatedly extracted with boiling carbon tetrachloride which removed unchanged T.N.T. The residue (1·5 gm) was a brown amorphous solid of an indefinite melting point (above 200°).

3 gms of this photodecomposition product were dissolved in 20 ml. acetone and fractionally precipitated by adding carbon tetrachloride, and fractions collected when acetone/carbontetrachloride ratios were 1 : 3, 1 : 4 and 1 : 6. Yields 1·2 gm, 0·4 gm and 0·6 gm respectively.

Fraction from Acetone/CCl_4	Mol. Weight	N% (Microdumas)	NO_2%
1:3	1050—1300	15·24	37·2
1:4	850—900	..	35·5
1:6	880	15·72	32·1
T.N.T.	227	18·5	60·8

Experiment 2

Photodecomposition of nitrobenzene

3 ml. of pure redistilled nitrobenzene were suspended in about 400 ml. of 0·2 N NaOH (pH 12·6) and the solution was exposed to sunlight in a transparent quartz tube (the reaction was later found to take place in a glass tube also). After 10 days exposure the deep yellow aqueous phase was separated and neutralised with CO_2 (phenolphthalein, external). The solution was then extracted with ether, the ether extract was washed with water and extracted with N/10 alkali. The alkali extract was treated with an excess of saturated $NaHCO_3$ solution and distilled, about 30 ml of distillate being collected. The distillate was extracted with ether, ether extract dried over sodium sulphate and ether distilled off. The residue was an oily liquid with a distinct smell of phenol. It gave a positive test with Millons reagent and with Ferric chloride. The material was further identified as phenol through its tribromo derivative, m.p. 95°.

p-Cresol was similarly isolated, after exposure of paranitrotoluene. In this case steam distillation was not necessary, as the cresol crystallised directly from the ether extract residue. Identity of the p-cresol was confirmed by preparing its 3 : 5 dinitrobenzoate m.p. 180° and benzoate m.p. 71°. Yield of crystalline p-cresol benzoate obtained in a separate similar experiment was 25 mgms.

Experiment 3

Photodecomposition of 1 : nitronaphthalene

(a) Isolation of 1-naphthol

5 gms of pure 1-nitronaphthalene were suspended in 400 ml. of 0·2 N NaOH and exposed to sunlight for 10 days. The solution was filtered from unchanged nitronaphthalene and the filtrate treated as in Expt. 1, except that the alkali soluble photodecomposition product were finally taken up in benzene instead of ether. The benzene solution was washed free from acid and dried over sodium sulphate.

The benzene extract was chromatographed over an alumina column (10 cm long, 14 mm diam). The colourless benzene elutate was shaken with three 50 ml. portions of N/10 alkali. The alkali extract was acidified with sulphuric acid and extracted with ether. Residue from this ether extract was a white crystalline solid. Yield 50 mgm. A small portion of the solid was purified by sublimation on a microscope coverglass, m.p. 94°. The solid was identified as 1-naphthol by mixed m.p. and by the preparation of 2 : 4 dinitro-1-naphthol m.p. 137° as a derivative. The crude 1-naphthol gave a distinct green fluorescence when its solution in 1 : 1 Conc. H_2SO_4/acetic acid was exposed to ultraviolet light indicating the presence of a trace of 2-naphthol.[19] 2-naphthol was similarly isolated from the photodecomposition products of 2-nitronaphthalene.

(b) Isolation of 4-nitroso-1-naphthol

The lemon yellow band which appeared as the bottommost band on the chromatographic column above, was mechanically separated and extracted with ether in the presence of a small quantity of dil. sulphuric acid. The ether extract was shaken with three 20 ml. portions of N/5 alkali. The alkali extract on acidification gave a pale yellow solid. This was crystallised from benzene in pale yellow needles, m.p. 195-200° with decomposition. Yield 15 mgm. This product was identified as 4-nitroso-1-naphthol by mixed melting point with 4-nitroso-1-naphthol prepared by Goldschmidt's [20] method, and by preparing 4-nitro-1-naphthol m.p. 164° as a derivative.

Incidentally it has been found that the 4-nitroso-1-naphthol prepared by Goldschmidt's[20] method could be more easily isolated in a pure form, if a benzene solution of the reaction product was chromatographed on alumina.

(c) Isolation of 2-nitroso-1-naphthol

About 1200 ml. of a suspension of pure 1-nitro-naphthalene (15 gms) in 0·2 N NaOH were exposed to sunlight for 15 days in three glass tubes. A benzene extract of the alkali soluble photodecomposition products was prepared as in (*a*) above. This extract was passed through an alumina column (14 mm diam, 15 cm. long) the column was successively washed with 50 ml. benzene, 50 ml. 75/25 benzene/alcohol and 50 ml. alcohol. A reddish yellow band was, now left on the column just below the top. The column was now washed with 100 ml. ether containing 1 ml. acetic acid, when a deep yellow elutate was obtained. On evaporation this gave a reddish yellow crystalline residue which when crystallised from alcohol gave a yellow crystalline solid on long standing, m.p. 160-162°. This solid gave a blood red colouration with conc. sulphuric acid indicating that it was 2-nitroso-1-naphthol. The identity was confirmed by oxidising the material with hydrogen peroxide in N/10 alkali solution, to 2-nitro-1-naphthol. m.p. 127°.

Experiment 4

Preparation of pure 1-nitro-napthalene free from 2-nitro-naphthalene

(a) Preparation of 1 : 5 dinitronaphthalene

A mixture of dinitronaphthalenes was obtained by nitrating 1-nitronaphthalene m.p. 54-55° by mixed acid below 10°. This was dissolved in 6 times its weight of hot pyridine. The pyridine solution on cooling deposited 1 : 5 dinitronaphthalene. This was further crystallised from glacial acetic acid, m.p. 217°.

(b) 1-nitro, 5-amino-naphthalene

12 gms of finely powdered pure 1 : 5 dinitronaphthalene were suspended in 100 ml. of ethyl alcohol and 10 ml. of Ammonia (d=0·88) were added. Hydrogen sulphide was then passed through the mixture till all the dinitronaphthalene was dissolved. The yellow solid precipitated during the reduction could easily be distinguished from the dinitronaphthalene. The mixture was then poured in water when a red brown solid separated. This was extracted with 200 ml. of hot dilute HCl (1 : 3). The acid extract was filtered and made alkaline with ammonia. The precipitated solid was used further without purification.

(c) 1-nitronaphthalene

7 gms of crude 1-nitro-5-amino naphthalene were dissolved in 200 ml. alcohol and 10 gms of conc. sulphuric acid were added. The solution was cooled to 5° and a cold 40% solution of sodium nitrite was slowly added in slight excess (Strach iodide, external). About 11·5 ml. were required. The mixture was refluxed on a water-bath for 2 hours and bulk of the alcohol was then distilled off. The residue was distilled with steam. The solid in the distillate was filtered, washed with water and 0·2 N alkali. Yield 2 gms. The material was heated on a water bath to allow sublimation of any naphthalene present. Heating was stopped when a crystalline yellow sublimate appeared. The residue was crystallised from alcohol and then from petroleum ether. It crystallised in the form of fine golden yellow needles. m.p. 56·5° (Corr.)

Thanks are due to the Superintendent of Development, Technical Development Establishment (Military Explosives), Kirkee, for his keen interest and to the Director of Technical Development, Army Headquarters, M.G.O's Branch, New Delhi for permission to publish the results.

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