485. *The Reaction of Nitrogen Dioxide with Some Methylnitroanilines.*

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The reaction of *N*-methyl-*o*- and -*p*-nitroaniline and some related compounds with nitrogen dioxide, in solution and in the solid state, has been investigated, and their ultraviolet absorption spectra are recorded. The reaction usually gives *N*-methyl-2 : 4-dinitroaniline as the main product: its mechanism is discussed

Nitric esters are thermally unstable, liberating nitrogen dioxide and, in the later stages of reaction, also nitric oxide and nitric acid. At constant temperature, breakdown of the ester proceeds at a constant rate, so long as the nitrogen dioxide is removed from the system. Phillips [1] has shown that, in the gas phase, nitrogen dioxide in small amounts inhibits the breakdown of nitric esters, presumably by reversal of the primary step. For solid or liquid nitric esters, however, there is evidence that, in the absence of a stabiliser which will react preferentially with the nitrogen dioxide formed, thermal decomposition becomes autocatalytic. The autocatalysed step is postulated as hydrolysis catalysed by acid formed from nitrogen dioxide in the initial stages of decomposition. In the presence of a stabiliser which will react preferentially with nitrogen dioxide or acid, or both, the rate of decomposition should be constant and a function only of temperature. As in practical systems of nitric esters containing stabiliser, the nitric ester is in large excess, the rate of disappearance of stabiliser will also be sensibly constant, and the kinetics of the overall reaction of pseudo-zero order. The stabilisation proceeds by at least two steps, of which the rate-determining one is considered to be the breakdown of the nitric ester, according to the scheme:

$$\mathrm{RO{\cdot}NO_2} \rightleftharpoons \mathrm{RO{\cdot}} + \mathrm{NO_2}\ \text{(Slow)}$$

$$\mathrm{NO_2} + \text{Stabiliser} \longrightarrow \text{Products (Fast)}$$

Similar reactions have been studied by Hughes, Ingold, and their co-workers [2-6] in the nitration of aromatic amines and the rearrangement of aromatic nitroamines.

In order to study the steps involved in the stabilisation, the action of nitric oxide and of nitrogen dioxide on *N*-methyl-*o*- and -*p*-nitroaniline was examined.

Results

At temperatures up to 50°, dry nitric oxide did not react with *N*-methyl-*p*-nitro- (I), -*p*-nitro-*N*-nitroso- (II), or -*p* : *N*-dinitro-aniline (IV), either in the solid state or in solution. In the presence of added water, a solution of *N*-methyl-*p*-nitroaniline in dioxan slowly absorbed nitric oxide to give *N*-methyl-*p*-nitro-*N*-nitrosoaniline. Moist nitric oxide was without effect on either the nitrosamine or the related nitramine. Similar results were obtained with *N*-methyl-

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[1] Phillips, *Nature*, 1947, **160**, 753.
[2] Glazer, Hughes, Ingold, James, Jones, and Roberts, *J.*, 1950, 2657.
[3] Hughes and Jones, *J.*, 1950, 2678.
[4] Blackall and Hughes, *Nature*, 1952, **170**, 972.
[5] Brownstein, Bunton, and Hughes, *Chem. and Ind.*, 1956, 981.
[6] *Idem.*, *J.*, 1958, 4354.

o-nitroaniline and its derivatives. Addition of as little as 1% of nitrogen dioxide to the dry nitric oxide very markedly increased both the rate and the extent of reaction with solutions of *N*-methyl-*p*-nitroaniline in nitromethane or dioxan, the main products being *N*-methyl-*p*-nitro-*N*-nitrosoaniline (II) and *N*-methyl-2 : 4-dinitroaniline (VI), together with small quantities of materials which could not be identified with certainty. These results are in accord with those of early workers who used "nitrous fumes" to nitrate aromatic amines. More recently, Glazer *et al.*[2] prepared *N*-methyl-2 : 4-dinitro- and -2 : 4 : 6-trinitro-*N*-nitrosoaniline by the action of oxides of nitrogen on solutions of the corresponding amines in acetic acid.

Reaction of a solution of *N*-methyl-*p*-nitroaniline in glacial acetic acid with excess of nitrogen dioxide at 0° for 96 hours gave the dinitro-amine (VI) and -nitrosamine (V) in 77 and 11% yield respectively, together with a small quantity of *p*-nitro-nitrosamine (II). Reaction at 100° for 30 minutes gave the dinitro-amine and -nitrosamine in 89 and 6% yield respectively. Reaction of two mol. of nitrogen peroxide at 0° or 100° gave the *p*-nitro-nitrosamine in over 90% yield.

Reaction of *N*-methyl-*p*-nitroaniline in dioxan with nitrogen dioxide was studied quantitatively at 25°. One mol. of amine rapidly reacted with two mol. of nitrogen dioxide to give one of *N*-methyl-*p*-nitro-*N*-nitrosoaniline and one of nitric acid; this is explained by consideration of the ionisation of nitrogen dioxide in solution:

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+\cdot NO_3^-$$

$$p\text{-}NO_2\cdot C_6H_4\cdot NHMe + N_2O_4 \longrightarrow [p\text{-}NO_2\cdot C_6H_4\cdot NHMe\cdot NO]^+NO_3^-$$

On further reaction, two mol., and finally nearly three, of dinitrogen tetroxide were absorbed, with progressively slower reaction. The main products were *N*-methyl-2 : 4-dinitroaniline and *N*-methyl-*p*-nitro-*N*-nitrosoaniline. Similar results were obtained for reaction of *N*-methyl-*o*-nitroaniline in dioxan: the main products were the 2 : 4-dinitro-amine and dinitro-nitrosamine, and no 2 : 6-dinitro-amine was found. The last result was unexpected, as *N*-methyl-2 : *N*-dinitroaniline undergoes acid-catalysed rearrangement to give *N*-methyl-2 : 4- and -2 : 6-dinitroaniline in approximately equal amounts.

A solution of *N*-methyl-*p*-nitro-*N*-nitrosoaniline in nitromethane with nitrogen dioxide for 24 hours at 35° gave 20% of *N*-methyl-2 : 4-dinitroaniline, and 80% of unchanged nitrosamine. After 7 days at 35^c, the main products were *N*-methyl-2 : 4-dinitro- and -4 : *N*-dinitroaniline. Transitory formation of the 2 : 4-dinitro-nitrosamine (V) was also observed. In 18 hours at 75°, stoicheiometric amounts of nitrogen dioxide quantitatively converted *N*-methyl-*p*-nitro-*N*-nitrosoaniline into *N*-methyl-2 : 4-dinitroaniline. With a considerable excess of nitrogen dioxide, solutions of *p*-nitro-nitrosamine, *p*-nitro-nitramine, 2 : 4-dinitro-amine, and 2 : 4-dinitro-nitrosamine in nitromethane were quantitatively converted into *N*-methyl-2 : 4 : 6-trinitro-aniline (VII) in 18 hours at 75°. The probable course of reaction was oxidation of the nitrosamines to the nitramines, followed by rearrangement to the ring nitro-compound, although under preparative conditions Hughes, Ingold, *et al.*[2] failed to oxidise the 2 : 4-dinitro-nitrosamine to the dinitro-nitramine. Hughes, Ingold, and Pearson [7] have recently shown that *N*-methyl-2 : 4-dinitroaniline and *N*-methyl-2 : 4 : *N*-trinitroaniline are converted into the 2 : 4 : 6-trinitro-nitramine by nitric acid in nitromethane at 25°, by *N*-nitration followed by rearrangement to *N*-methyl-2 : 4 : 6-trinitroaniline and subsequent *N*-nitration. Under conditions of considerable excess of nitrogen dioxide in nitromethane at 75°, compounds (II), (IV), (V), and (VI) may have undergone similar nitration and rearrangement, after denitrosation of compounds (II) and (V). However, the absence of the 2 : 4 : 6-trinitro-nitramine in our products makes this route less likely than that given above.

The nitramine rearrangement of *N*-methyl-*o* : *N*- and -*p* : *N*-dinitro- and -2 : 4 : *N*- and -2 : 6 : *N*-trinitroaniline was found to proceed smoothly in strong aqueous sulphuric acid and in acetic acid catalysed by sulphuric acid. This type of rearrangement has previously been studied in some detail by Bradfield and Orton,[8] and by Hughes, Ingold, and their co-workers [2–4] who have shown that the rearrangement is intramolecular, although the work of Hughes and Jones [3] and of Clark, Holden, and Malkin [9] has shown that in the presence of a suitable acceptor some intermolecular rearrangement takes place, by acidolysis of the nitramine and subsequent ring-nitration.

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[7] Hughes, Ingold, and Pearson, *J.*, 1958, 4357.

[8] Bradfield and Orton, *J.*, 1929, 917.

[9] Clark, Holden, and Malkin, *J.*, 1950, 1556.

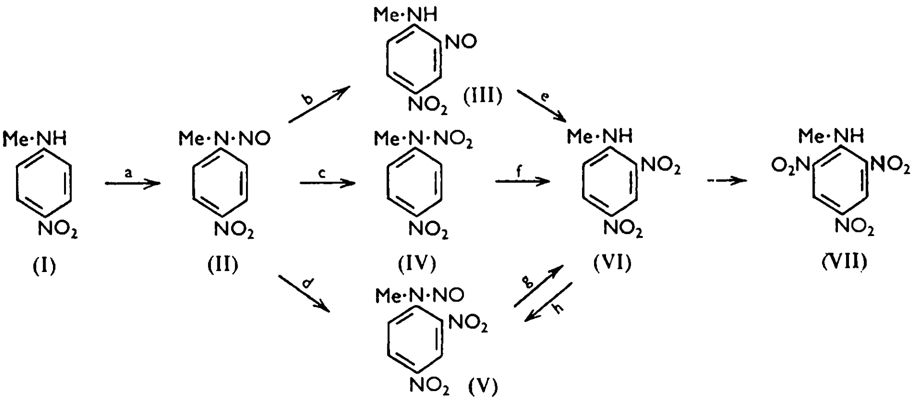
The rearrangement of *N*-methyl-*p* : *N*-dinitro- to *N*-methyl-2 : 4-dinitro-aniline failed in normal aqueous perchloric acid, although Robinson [10] claimed that in perchloric acid nitration was faster than in sulphuric acid. In 0·2N-sulphuric acid in nitromethane, the rearrangement was quantitative and very fast. Similar results were obtained for the rearrangement of *N*-methyl-2 : 4 : *N*-, and -2 : 6 : *N*-trinitroaniline to *N*-methyl-2 : 4 : 6-trinitroaniline, indicating that the rearrangement is dependent on the acidity function of the medium, and not on the stoicheiometric acidity. Hughes, Ingold, and Pearson [7] noted this increase in rate in the presence of sulphuric acid, and also that addition of sodium perchlorate to the reaction mixture increased the rate, but not to the same extent as did sulphuric acid.

After *N*-methyl-*p*-nitroaniline had been heated with nitrocellulose at 80° for periods up to 30 days, the products were mainly *N*-methyl-2 : 4-dinitroaniline and *N*-methyl-*p*-nitro-*N*-nitrosoaniline. Traces of a third compound of unknown spectrum were also formed. This is tentatively considered to be *N*-methyl-4-nitro-2-nitrosoaniline (III), by analogy with the rearrangement of *N*-nitrosodiphenylamine to *C*-nitrosodiphenylamine found by Pauling [11] under similar conditions. Only very small quantities were formed, and confirmation proved impossible. Fischer and Hepp [12] described the rearrangement of *N*-methyl-*N*-nitrosoaniline to *N*-methyl-*p*-nitrosoaniline. Attempts to rearrange *N*-methyl-*p*-nitro-*N*-nitrosoaniline to the 2-nitroso-compound (III) under similar conditions failed. This result was not unexpected, as nitrosation is not a vigorous electrophilic process, and the presence of the nitro-group in the ring would cause it to be heavily deactivated to electrophilic attack. Similarly, attempts to rearrange *N*-methyl-2 : 4-dinitro-*N*-nitrosoaniline failed.[2] The failure of *N*-methyl-2 : 4-dinitroaniline to form a nitrosamine under the conditions which gave the 2 : 4 : 6-trinitro-nitrosamine is in line with the observation that *N*-methyl-2 : 4-dinitroaniline is more slowly nitrated than *N*-methyl-2 : 4 : 6-trinitroaniline.[7]

All the nitrosamines described in this work were photosensitive in solution. *N*-Methyl-2 : 4- and -2 : 6-dinitro-*N*-nitrosoaniline were particularly photosensitive in solution, and to a smaller extent in the solid state.

DISCUSSION

The initial reaction of nitrogen dioxide with *N*-methyl-*p*-nitroaniline (I) gave the nitrosamine (II) quantitatively, one mole of nitric acid being produced for each mole of dinitrogen tetroxide which reacted. The following scheme outlines the possible sequences of reaction:



Step (a), the formation of compound (II), appears to be unequivocal. At 75°, compound (II) was quantitatively converted into compound (VI) by nitrogen dioxide in nitromethane. Thus compound (VI) may be formed by route (c) and (f) or route (d) and (g). Compound (VI) could also be formed by route (b) and (e), although preparatively reaction (b) could not be carried out. The observation of a compound of unknown spectrum,

[10] Robinson, *J.*, 1941, 238.
[11] Pauling, O.S.R.D. Report No. 4431.
[12] Fischer and Hepp, *Ber.*, 1886, **19**, 370.

tentatively identified as compound (III), leaves the possibility of route (b) and (e) open. The nitramine rearrangement, route (f), failed in aqueous perchloric acid, although it was very fast in the presence of a small quantity of sulphuric acid in nitromethane. Denitrosation (g) was rapid in the presence of light, but its reverse (h) could only be carried out under forcing conditions, the use of nitrososulphuric acid. In reactions (f) and (h) the most important consideration is the acidity function of the medium, and the available evidence indicates that it is high in a solution of nitrogen peroxide in nitromethane.

With an excess of nitrogen dioxide, in nitromethane solution at 75°, compounds (II), (IV), (V), and (VI) were all quantitatively converted into the final product (VII). The appearance of compound (IV) in the reaction of nitrogen peroxide with compound (II) at 35° indicates that the overall reaction consists of formation of the nitrosamines followed by oxidation to the nitramines and rearrangement to the ring nitro-compounds. Under conditions where nitrogen dioxide is not in excess, the reaction probably proceeds by ring-nitration (d) by the nitric acid produced during the reaction, with prior or subsequent denitrosation.

The hypothesis of ring-nitration is supported by the observations on the absorption of nitrogen dioxide by solutions of *N*-methyl-*o*-nitroaniline. In this case, no *N*-methyl-2 : 6-dinitroaniline or its derivatives were found among the products. At 25°, the probable course of the reaction was formation of *N*-methyl-*o*-nitro-*N*-nitrosoaniline, and subsequent direct ring-nitration to *N*-methyl-2 : 4-dinitro-*N*-nitrosoaniline (V), which was unstable in light and readily decomposed to give *N*-methyl-2 : 4-dinitroaniline (VI). Sterically, the *o*-nitro-nitrosamine is unlikely to undergo nitration in the 6-position, although the intramolecular rearrangement of *N*-methyl-*o* : *N*-dinitroaniline has been shown to yield approximately 50% of *N*-methyl-2 : 6-dinitroaniline, and intramolecular rearrangement of *o* : *N*-dinitroaniline gave almost entirely 2 : 6-dinitroaniline.[13]

By analogy, the absence of any compound of *N*-methyl-2 : 6-dinitroaniline constitutes strong evidence for rejecting route (c) and (f), and leaves route (d) and (g) as being the only reasonably practicable route to compounds (VI) and (VII) from compound (I).

EXPERIMENTAL

Reference Compounds.—The following compounds were prepared by standard methods. M. p.s are corrected; those in parentheses are as recorded elsewhere.

N-Methyl-*o*-nitroaniline, tangerine-coloured needles (from pentane–ether), m. p. 37° (37° [14]) (yield 89%).

N-Methyl-*p*-nitroaniline, light yellow prismatic needles (from alcohol or benzene), m. p. 152—153° (152° [14]) (yield 93%).

N-Methyl-2 : 4-dinitroaniline, canary-yellow needles (from acetone or acetic acid), m. p. 179—180° (178° [15]) (98%).

N-Methyl-*o*-nitro-*N*-nitrosoaniline, yellow needles [from methanol–light petroleum (b. p. 40—60°)], m. p. 36° (36° [16]) (87%).

N-Methyl-*p*-nitro-*N*-nitrosoaniline, creamy yellow needles (from ethanol), m. p. 102—103° (100° [17]) (95%). This and the *ortho*-analogue slowly decomposed to the parent amines in boiling ethanol.

N-Methyl-2 : 4-dinitro-*N*-nitrosoaniline could not be prepared by the method of Stoermer and Hoffman.[18] It was prepared by treatment of a solution of *N*-methyl-2 : 4-dinitroaniline in 98% sulphuric acid with a solution of nitrososulphuric acid in the same solvent. It formed light yellow plates (from ethanol), m. p. 85—86° (85° [9]) (60%). In boiling alcohol it rapidly decomposed to the parent amine.

N-Methyl-*o* : *N*-dinitroaniline, pale yellow prisms (from methanol–light petroleum), m. p. 67—68·5° (67° [13]) (76%).

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[13] Bamberger and Voss, *Ber.*, 1897, **30**, 1256.

[14] Blanksma, *Rec. Trav. chim.*, 1902, **21**, 272.

[15] Leymann, *Ber.*, 1882, **15**, 1235.

[16] Hempel, *J. prakt. Chem.*, 1884, **41**, 168.

[17] Meldola and Salmon, *J.*, 1888, **53**, 776.

[18] Stoermer and Hoffman, *Ber.*, 1898, **31**, 2530.

N-Methyl-*p* : *N*-dinitroaniline, creamy-coloured needles (from benzene–light petroleum), m. p. 140—142° (140°[19]) (65%).

N-Methyl-2 : 4 : *N*-trinitroaniline, very light yellow cubes (from alcohol–benzene), m. p. 114·5—116° (115°[9]) (90%).

N-Methyl-2 : 4 : 6-trinitroaniline, yellow needles (from alcohol), m. p. 114—115° (113—114°[9]) (95%).

N-Methyl-2 : 4 : 6-trinitro-*N*-nitrosoaniline, light yellow prisms (from alcohol), m. p. 106—107° (106·5°[20]) (85%).

N-Methyl-2 : 4 : 6 : *N*-tetranitroaniline, colourless prisms (from alcohol), m. p. 130—131° (131—132°[21]) (85%).

Rearrangement of *N*-methyl-*o* : *N*-dinitroaniline in concentrated sulphuric acid at 0° gave a mixture of *N*-methyl-2 : 4- and -2 : 6-dinitroaniline. *N*-Methyl-2 : 6-dinitroaniline was soluble in boiling light petroleum (b. p. 40—60°); it formed light orange-yellow needles [from alcohol–light petroleum (b. p. 60—80°)], m. p. 106—107° (106°[13]) (33%). The residue of *N*-methyl-2 : 4-dinitroaniline (36%) formed orange-red needles, m. p. 179—180°, from glacial acetic acid, identical in m. p. (mixed m. p.) and ultraviolet absorption with the yellow form previously described.

Under similar conditions, *N*-methyl-*p* : *N*-dinitroaniline smoothly rearranged to *N*-methyl-2 : 4-dinitroaniline.

N-Methyl-2 : 6-dinitro-*N*-nitrosoaniline formed very pale yellow needles (70% yield) [from alcohol or alcohol–light petroleum (b. p. 80—100°)], m. p. 115—116° (115—116°[22]). It did not decompose in boiling alcohol in the dark, but was very prone to photolytic decomposition in solution and to a smaller extent in the solid state. It partly reverted to *N*-methyl-2 : 6-dinitroaniline and partly underwent oxidation.

N-Methyl-2 : 6 : *N*-trinitroaniline, white needles (from alcohol or aqueous alcohol), m. p. 111—112°, was prepared (85%) by treatment of *N*-methyl-2 : 6-dinitroaniline nitrate with acetic anhydride at 0°. The mixed m. p. with the 2 : 4 : *N*-analogue (m. p. 114·5—116°) was 83—85°. The structure was confirmed by removal of the *N*-nitro-group in hot phenol, which yielded *N*-methyl-2 : 6-dinitroaniline (cf. refs. 9 and 23).

N-Methyl-2 : 4 : *N*- and -2 : 6 : *N*-trinitroaniline rearranged smoothly in concentrated sulphuric acid to *N*-methyl-2 : 4 : 6-trinitroaniline.

Experimental Techniques.—Nitrogen dioxide, purified by repeated distillation of a commercial sample in a stream of oxygen, was a pure white solid, m. p. −9·5°. Nitric oxide was prepared by decomposition of the ferrous sulphate–nitric oxide complex. All solvents were dried and redistilled.

Solutions of nitrogen dioxide were made up in the solvents, and analysed for nitrogen dioxide content and acidity by standard methods, with an accuracy for synthetic mixtures of nitric acid and nitrogen dioxide in solvent of $\pm<1\%$. The presence of nitrosamines and nitramines did not interfere if the solutions were cold and titrated within 30 min. In alkaline solution, however, hydrolysis occurred on warming or on long standing, giving a high figure for the total acidity. Quantitative measurements were not made of total acidity in solutions of nitrogen dioxide in acetic acid or nitromethane.

The reaction of nitrogen dioxide with the methylnitroanilines was studied by heating solutions in sealed Pyrex tubes and followed in quantitative runs by measuring the fall in nitrogen dioxide and increase in nitric acid content. In qualitative runs, the amount of nitrogen dioxide consumed was measured at the end of the reaction period only. After reaction, the solution was neutralised with calcium carbonate and evaporated to dryness in darkness *in vacuo* at 40—50°, and the products were separated chromatographically, usually in 1 : 1 benzene–light petroleum, on a silicic acid–Celite 535 column wrapped in black paper to prevent photolytic decomposition. The decreasing order of absorption was *N*-methyl-2 : 4-dinitroaniline, its nitrosamine, the *p*-nitro-nitrosamine, the *p*-nitro-nitramine, the *p*-nitro-amine, the trinitro-amine. Identities were established by ultraviolet spectra in 95% ethanol.

The reaction of nitric oxide was followed manometrically, a solution of the compound under

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[19] Bamberger and Dietrich, *Ber.*, 1897, **30**, 1254.

[20] Bamberger and Müller, *Ber.*, 1900, **33**, 103.

[21] Franchimont, *Rev. Trav. chim.*, 1910, **29**, 302.

[22] Meldola and Hollely, *J.*, 1915, **107**, 619.

[23] Mertens, *Ber.*, 1886, **19**, 2123; van Romburg, *Rec. Trav. chim.*, 1886, **5**, 140.

nitric oxide being stirred in a calibrated vessel in a thermostat. The products were separated chromatographically and identified as before.

The nitrocellulose containing *N*-methyl-*p*-nitroaniline was prepared by swelling nitrocellulose in alcohol–ether, and adding to it a solution of the amine in alcohol. The solvent was removed at 45°. The dry solid was shredded and aged in sealed containers at 80°. The products were extracted from the nitrocellulose with methylene chloride. The solution was neutralised and evaporated, and the products were separated, and identified as before.

Ultraviolet Spectra.—Ultraviolet absorption spectra were measured on a Unicam S.P. 500 ultraviolet spectrophotometer, for 0·001% solutions in 95% ethanol. The spectra of the nitrosamines were also determined for hexane solutions but did not differ from those of freshly prepared solutions in ethanol. The main characteristics are given in the annexed Table.

Ar·NMeX		$\lambda_{max.}$	$\lambda_{min.}$	$D_{max.}/$			Ar·NMeX		$\lambda_{max.}$	$\lambda_{min.}$	$D_{max.}/$		
NO_2 in Ar	X	(mμ)	(mμ)	$D_{min.}$*	*C*/*D* †	$10^{-3}\varepsilon$	NO_2 in Ar	X	(mμ)	(mμ)	$D_{min.}$*	*C*/*D* †	$10^{-3}\varepsilon$
o-	H	231	265		0·71	21·4	2 : 4-	H	260	245	1·17	2·34	16·18
		280	317—	1·35	3·26	4·65			346	290	10·9	1·23	
			319				2 : 4-	NO	215			1·45	14·5
o-	NO	240	228	1·02	1·54	11·76	2 : 4-	NO_2	215	222	1·03	1·55	15·95
o-	NO_2	245	234	1·14	1·89	10·4	2 : 6-	H	234	305		1·11	17·8
p-	H	230	280	24·75	2·06	18·3	2 : 6-	NO	239			1·57	14·43
		386			0·83		2 : 6-	NO_2	228	220	1·02	1·38	17·55
p-	NO	220	250	7·77	1·69	15·0	2 : 4 : 6-	H	335	282	6·92	1·61	15·0
		312			1·21		2 : 4 : 6-	NO	215			1·20	22·4
p-	NO_2	213	242	1·61	1·79	8·3	2 : 4 : 6-	NO_2	220			1·21	23·8
		289			2·37								

* The ratio of the optical density of the maximum to the optical density of the next minimum of shorter wavelength.

† The ratio of the concentration of the solution (mg./100 ml.) to the optical density of the maximum (10 mm. cell).

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