66. *The Action of Phenylhydrazine and of Thiourea on Aliphatic Nitro-compounds.*

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PREVIOUS work by one of us (J., 1920, **117**, 880; 1922, **121**, 892) showed that, whereas the acid reduction of tetranitromethane yielded guanidine in the cases examined, alkaline reducing agents eliminated a nitro-group, a salt of nitroform being produced. Phenylhydrazine behaved abnormally and carried the reaction beyond the nitroform stage: and this reaction has now been further examined. The oxidation of phenylhydrazine yields various products under different conditions. E. Meyer (*J. pr. Chem.*, 1887, **36**, 115) showed that with iodine in excess, iodobenzene is formed and nitrogen liberated, the reaction forming the basis of a method for the estimation of phenylhydrazine; but in other circumstances aniline and diazobenzeneimide are produced: or diazobenzene-phenylhydrazide may be formed (Stollé, *ibid.*, 1902, **66**, 335). Hydrogen peroxide leads to the formation of benzene and diazobenzeneimide (Wuster, *Ber.*, 1887, **20**, 2633), but quinones (Clauser, *Ber.*, 1901, **34**, 889), and under certain conditions the halogens (*Ber.*, 1885, **18**, 90, 786; 1892, **25**, 1074) and alkaline hypochlorite (de Coninck, *Compt. rend.*, 1898, **126**, 1043; **127**, 1028), liberate nitrogen quantitatively by the breakdown of the phenylhydrazine. There is therefore an element of uncertainty in any method which relies on the quantitative liberation of nitrogen from this reagent.

Gasometric estimations show that approximately three molecules of nitrogen are liberated by 1 g.-mol. of tetranitromethane when it is reduced by phenylhydrazine in the presence of alkali. If the reagent is oxidised to benzene, one molecule of nitrogen is set free for each molecule of hydrogen becoming available for reduction, and the result is most simply explained by assuming the reduction to involve the successive elimination of nitro-groups with the ultimate formation of nitromethane :

$$C(NO_2)_4 + 3C_6H_5{\cdot}NH{\cdot}NH_2 + 4KOH = CH_2{:}NO{\cdot}OK + 3C_6H_6 + 3N_2 + 3KNO_2 + 4H_2O.$$

Walther (*J. pr. Chem.*, 1896, **53**, 433) showed that aromatic nitro-compounds are readily converted into the corresponding amino-compounds when heated with phenylhydrazine in an autoclave; but nitromethane and nitroethane are attacked only with difficulty. We find that nitromethane is stable towards phenylhydrazine under the conditions of reduction described in this paper : for only a trace of nitrogen is evolved during 4 days. It is therefore not unreasonable to consider nitromethane as an end-product of the reductions considered.

On account of the uncertainty of nitrogen estimations already pointed out, further support for the suggested course of the reaction is desirable. According to the equation the eliminated nitro-groups are fixed as potassium nitrite, and a second method of estimation is thus open. Determinations of the amount of nitrite present in the reaction mixtures by urea and thiourea were found to be in fair agreement with the theoretical values.

Final proof of the course of the reaction would be afforded by the isolation of nitromethane, but this has not been satisfactorily accomplished. The alkaline solution after removal of excess phenylhydrazine and benzene contains the nitromethane in presence of potassium nitrite : and acidification under these conditions results in the conversion of the nitro-compound into the unstable methylnitrolic acid (Tscherniak, *Annalen*, 1876, **180**, 166; V. Meyer and Constam, *ibid.*, 1882, **214**, 334). Alternative treatment led to the isolation of a small amount of nitromethane, identified as the potassium salt : the salt of an unidentified nitro-compound was also separated.

Griffith and Hunter (J., 1924, **125**, 463) examined the effect of warming an alkaline solution of potassium nitroform with various reducing agents and failed to detect the presence of potassium dinitromethane at any stage of the reaction : but ammonia was in all cases evolved. It was suggested that the observations furnished an explanation of the large amounts of nitrogen recorded in our previous experiments with phenylhydrazine. The course of the reaction now suggested is at variance with their views, and in several large-scale reductions we estimated the amount of ammonia in solution and found it to be quite negligible. Under the conditions of our experiments there is therefore no evidence of a complete decomposition of the nitro-compound such as occurs on warming, and the results point to the elimination of nitro-groups as the main reaction.

The action of phenylhydrazine on chloro- and bromo-nitroform, dibromodinitromethane, and the potassium salts of nitroform, bromodinitromethane, and dinitromethane has also been examined. All evolve nitrogen on treatment with the reagent, and in all cases nitrite is present in the reaction mixture. The reduction of the dinitro-compounds is slow.

Although the association of the different lines of evidence provides a definite case for the course of reaction suggested, further support is desirable on account of the unsatisfactory isolation of nitromethane. Attention was therefore directed to thiourea as a reducing agent. If reduction involves the elimination of nitro-groups, the nitrous acid produced in neutral or weakly acidic solutions would react directly with the excess of thiourea : and accordingly this reagent would function both as the reducing medium and as the agent for estimation. Such expectations were realised and the results obtained support the course of reaction set out above.

The effect of oxidising agents on thiourea follows in general one of two courses, giving either urea and sulphuric acid (Maly, *Monatsh.*, 1890, **11**, 277) or formamidine disulphide (Storsch, *ibid.*, p. 452; Fichter and Wink, *Ber.*, 1912, **45**, 1373; Werner, J., 1919, **115**, 1168). Both sulphuric acid and formamidine disulphide were found in the reaction product of thiourea and tetranitromethane. When nitrous acid acts on thiourea, the disulphide together with nitric oxide may be formed (Storsch, *loc. cit.*),

$$2CSN_2H_4 + 2HNO_2 = NH_2{\cdot}C(\colon NH){\cdot}S{\cdot}S{\cdot}C(\colon NH){\cdot}NH_2 + 2NO + 2H_2O$$

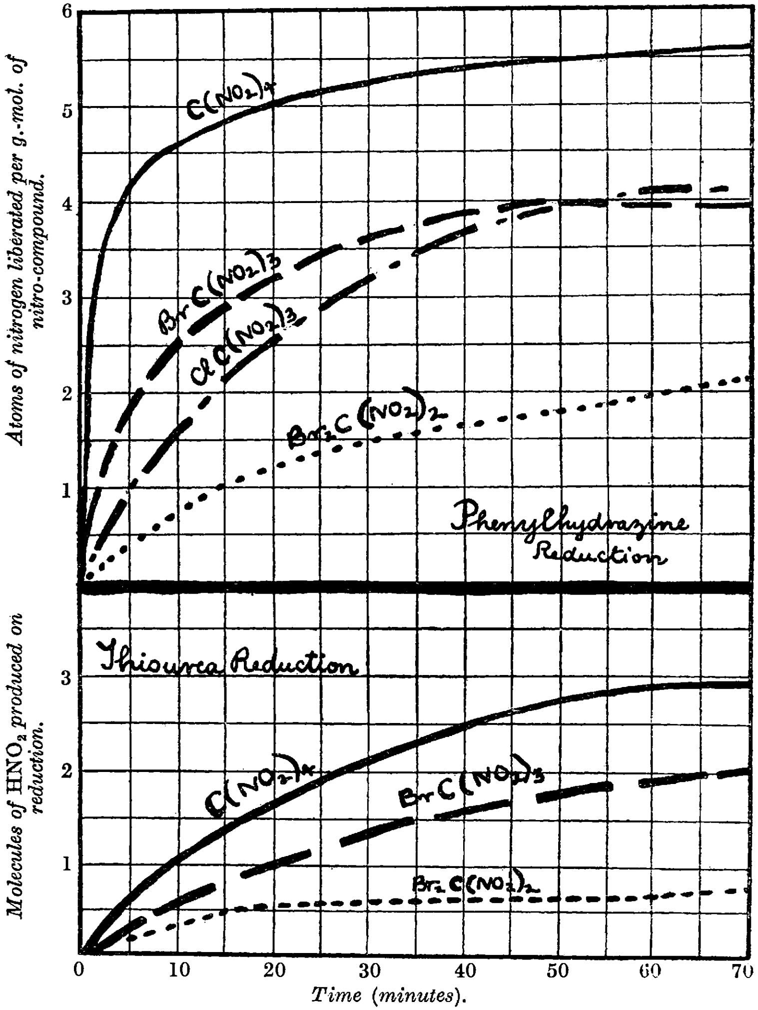
whereas in the presence of a weak acid the decomposition products are thiocyanic acid and nitrogen (Dixon, J., 1892, **61**, 526) :

$$CSN_2H_4 + HNO_2 = HCNS + N_2 + 2H_2O.$$

Werner (J., 1912, **101**, 2180) showed that the former course was followed only in the presence of a strongly ionised acid, and also pointed out that nitrous acid was capable of reacting in the absence of any other acid, the gaseous product being nitrogen. As a method of estimation it is immaterial which course the reaction takes, the volume of the gaseous product being unaffected : but since the gas evolved in the reaction with tetranitromethane consists essentially of nitrogen, it seems probable that the formamidine disulphide is produced in the initial reaction involving reduction of the nitro-compound :

$$C(NO_2)_4 + 6CSN_2H_4 = MeNO_2 + 3HNO_2 + 3C_2S_2N_4H_6.$$

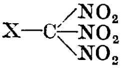
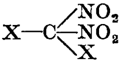
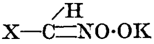
FIG. 1.



Analysis of the gases evolved in reactions with different nitro-compounds supports Coade and Werner's results (J., 1913, **103**, 1221) on the variation in composition of the gas when nitrous acid reacts in presence of acids of different strengths. Hydrobromic acid is present as a reaction product of bromonitroform, and nitric oxide (15%) is evolved together with nitrogen: dibromodinitromethane yields a gas still richer in nitric oxide (27—30%).

The preparation of the potassium salt of nitroform by the action of sodium ethoxide on tetranitromethane is not free from risk (Macbeth, *Ber.*, 1913, **46**, 2537). A convenient and safe method of preparation which we have used during the last 15 years is now described. This consists in shaking tetranitromethane with an aqueous solution of potassium hydroxide and glycerol. Pure crystals of the salt soon separate, all trace of tetranitromethane having disappeared in ½ hour. The oxidation products of the glycerol have not been examined, but the reaction will probably be found to bear a close analogy to the conversion into glycerose recorded by Fischer and Tafel (*Ber.*, 1887, **20**, 3384; 1888, **21**, 2634).

The rates of reaction in the reductions may be followed by measurement of the volume of gas evolved, and some such results are expressed in Fig. 1. The times taken to remove the first group in the phenylhydrazine experiments are set down for the series of compounds below: and these may be interpreted as showing that the greater the electropositive effect imposed on an atom or group, the more quickly is it removed in the reduction. Similar effects are seen in the thiourea reductions recorded in detail in the experimental part.

	X.	Time.		X.	Time.
 $\mathrm{X{-}C(NO_2)_3}$	NO_2	30 secs.	 $\mathrm{X{-}C(NO_2)_2X}$	Br	1 hr.
	Br	4 mins.			
	Cl	13 mins.			
 $\mathrm{X{-}C(NO_2){=}NO{\cdot}OK}$	NO_2	27 mins.	 $\mathrm{X{-}C(H){=}NO{\cdot}OK}$	NO_2	very slow
	Br	2 hrs.			

EXPERIMENTAL.

Nitrogen Estimations.—The nitro-compounds were prepared by standard methods and carefully purified. The estimations were carried out in a mercury-filled Lunge nitrometer, 5 c.c. of an alcoholic solution of known strength of the nitro-compound being introduced, followed by 5 c.c. each of alcoholic phenylhydrazine (10%) and aqueous potassium hydroxide (20%). Typical results from a large number of experiments are recorded below, and approximately six atoms of nitrogen are seen to be liberated by g.-mol. quantities of bromonitroform and tetranitromethane. Chloronitroform gives a somewhat low result; two groups are eliminated in the course of an hour, but the third group is much more slowly removed, 5·5 atoms of nitrogen being liberated per g.-mol. of the nitro-compound after some 40 hours.

In the case of potassium bromodinitromethane and potassium nitroform definite weights are washed into the nitrometer with water, and the other reagents added. The reaction takes place slowly, but after standing, the nitrogen liberated exceeds the theoretical quantity : no inference can therefore be drawn from these experiments, but the nitrite determinations subsequently described and the reaction with thiourea indicate the removal of approximately one and two molecules of nitrous acid from the respective compounds. The times of reaction for the removal of the first group in these compounds (two atoms of N_2 liberated) found in a series of experiments are recorded in the table above, but the graphs are not shown in Fig. 1 on account of the excess of total nitrogen liberated.

Potassium dinitromethane was prepared by adding dibromodinitromethane (4 g.) to a solution of arsenious oxide (6 g.) and potassium hydroxide (12 g.) in water; after several hours, the solution was boiled for a short time and potassium dinitromethane, which separated on cooling, was twice recrystallised from water. The reduction of the nitro-compound by phenylhydrazine is comparatively slow, but nitrite estimations recorded later show that it is eventually complete. In a typical experiment 0·1288 g. of potassium dinitromethane liberated 0·67, 2·1, 4·16, 6·49, and 8·28 c.c. N_2 at N.T.P. after 0·95, 5·27, 24, 48, and 72 hours respectively; which correspond to 0·0674, 0·211, 0·418, 0·652, and 0·831 atoms of nitrogen per g.-mol. of potassium dinitromethane.

Substance.	Wt., g.	N_2 evolved (c.c.).	Temp.	Press., mm.	Atoms of N per g.-mol.
$C(NO_2)_4$	0·10049	37·0	12·6°	755·2	6·15
	0·10049	36·4	11·7	759·3	6·11
	0·10826	39·0	12·5	746·0	5·95
	0·10826	39·8	15·2	748·0	6·03
$CBr(NO_2)_3$	0·098	30·7	13·2	744	6·02
	0·098	30·5	11·4	746	6·03
$CCl(NO_2)_3$	0·9237	31·8	12·0	760	5·5
	0·9549	33·0	13·6	755	5·5

Nitrite Estimations.—In order to provide materials for these estimations and for the isolation of nitromethane, reductions were carried out on a larger scale. Tetranitromethane (10 g.), dissolved in alcohol (100 c.c.), was added in small quantities at 5-minute intervals to a solution of phenylhydrazine (30 g.) in alcohol (90%) containing potassium hydroxide (15 g.). The temperature was kept below 35°, and the mixture left over-night. After dilution with water and extraction with ether (10 times), the residual ether was removed by a current of air, the solution diluted to definite volume, and nitrite estimated in an aliquot part. In a typical experiment the final volume was 1120 c.c., and 10 c.c. of this gave an average of 32 c.c. of nitrogen at 15·5° and 757·2 mm. 10 G. of tetranitromethane therefore give rise to 12·89 g. of potassium nitrite, so 1 g.-mol. of the nitro-compound yields 2·97 mols. of potassium nitrite on reduction. In further experiments the values obtained lay between the limits 2·7 and 3·03 mols. of potassium nitrite. With bromonitroform an average value of 1·8 mols. of potassium nitrite was obtained, and with potassium dinitromethane, potassium bromodinitromethane, and potassium nitroform respectively 0·8, 0·7, and 1·5 mols. of potassium nitrite were detected. The reductions in these cases, however, are slow : and in a further reduction of potassium dinitromethane which was allowed to proceed for 5 days a value 1·02 mols. of potassium nitrite was obtained.

When dibromodinitromethane is reduced by adding it (4 g.) to an aqueous-alcoholic solution of phenylhydrazine and potassium hydroxide, a bromine atom is quickly removed (small-scale experiments showed on the average that a bromine atom is removed in 1 hour) and potassium bromodinitromethane precipitated. Further reduction occurs and after 5 days the precipitate consists essentially (90%) of potassium dinitromethane [Found : K, 26·2. $CHK(NO_2)_2$ requires K, 27·1%. $CBrK(NO_2)_2$ requires K, 17·5%]. When an alcoholic solution was used, the precipitate after 8 days' shaking consisted essentially (94%) of potassium bromide, and the amount of nitrite present in solution (0·63 mol. KNO_2 per g.-mol. of dibromodinitromethane) showed that the elimination of one of the nitro-groups had proceeded to a fair extent.

Ammonia Estimations.—No odour of ammonia was observed during any of the reactions described above, and examination of the solutions revealed the presence of traces only of ammonium salts. In a typical experiment the solution, freed from ether after extraction of the excess of phenylhydrazine, etc., was steam-distilled and the distillate (1500 c.c.) after acidification with hydrochloric acid was concentrated to 100 c.c. and cooled; platinic chloride (10%) was then added, and the crystalline precipitate collected after 24 hours (0·3335 g.) [Found : Pt, 43·9. $(NH_3)_2H_2PtCl_6$ requires Pt, 43·95%]. This corresponds to 0·027 g. of ammonia or only 0·53 g. per g.-mol. of tetranitromethane. In no experiment did the amount of ammonia estimated exceed 0·8 g. per g.-mol. of the nitro-compound. Ethereal extracts contained no ammonia in the cases examined.

Detection of Nitromethane.—Solutions prepared for nitrite estimation were examined for nitromethane with indifferent results. The free alkali was destroyed by passing carbon dioxide through the solution; alcohol was then distilled off, and the residual solution steam-distilled. Both distillates were evaporated under reduced pressure after the addition of potassium hydroxide, and the residue made faintly acid with sulphuric acid and extracted with ether. The extract was dried, and set aside after the addition of a few drops of potassium ethoxide, and the small amount of the salt which separated over-night was collected (Found : K, 38·9. $CH_2K{\cdot}NO_2$ requires K, 39·45%). Alternative treatment consists in adding excess of urea to the solution after ether extraction, and gradually acidifying the mixture with sulphuric acid. After aspiration of air, the product was steam-distilled, and the distillate made alkaline with potassium hydroxide (5 g.) and concentrated on the water-bath to about 50 c.c. Yellow crystals separated and on acidification, a white nitro-compound separated, which was filtered off. The filtrate was worked up for nitromethane, and the residue on the filter dissolved in ether. The solution, after being dried, soon deposited white rectangular needles (0·16 g.) of the unidentified nitro-compound. The substance is not a methane derivative, as it is a solid (m. p. 73—75°), and the intense yellow colour of the *potassium* salt suggests the presence of two nitro-groups attached to the same carbon atom (Found : K, 19·3%).

Thiourea Reductions.—These estimations were carried out in a mercury-filled Lunge nitrometer, 5 c.c. of an alcoholic solution of the nitro-compound being introduced, followed by 5 c.c. of an aqueous solution containing excess of thiourea (0·2 g.). The reactions were carried out with or without the addition of acetic acid and were mostly complete in 2 hours; but final readings were taken after 12 hours. Potassium salts were made up in aqueous solution, and glacial acetic acid (1 c.c.) was added after the thiourea. The results obtained in typical experiments are set out below, the last column (*A*) giving the mols. HNO_2 obtained from 1 mol. of the nitro-compound.

Substance.	Wt., g.	Gas evolved, c.c.	Temp.	Press., mm.	*A*.
$C(NO_2)_4$	0·04892	19·2	10·0°	746·0	3·26
	0·04892	18·7	9·6	742·5	3·17
	0·06270	26·0	12·0	721·0	3·30
$CBr(NO_2)_3$	0·05506	13·1	13·8	728	2·24
	0·05506	12·6	14·4	730	2·15
	0·11162	25·5	13·7	718	2·11
	0·09280	22·8	20·8	734	2·18
$CCl(NO_2)_3$	0·04452	13·7	16·9	733	2·32
$CK(NO_2)_3$	0·04624	11·1	16·6	770	1·95
$CBr_2(NO_2)_2$	0·1173	10·8	15·6	763	1·03
$CH_3{\cdot}CBr(NO_2)_2$	0·07076	8·4	22·2	760	0·98
$CH_3{\cdot}NO_2$	nil.				

The progressive liberation of nitrogen (or nitric oxide) is shown in the following examples.

Time, mins.	N_2 at N.T.P.	HNO_2, g. per g.-mol. of nitro-cmpd.	HNO_2, mol. per g.-mol.	Time, mins.	N_2 at N.T.P.	HNO_2, g. per g.-mol. of nitro-cmpd.	HNO_2, mol. per g.-mol.
Bromonitroform, 0·05506 g.							
2	0·77	6·78	0·14	75	11·38	100·2	2·13
5	2·01	17·70	0·38	105	11·7	103·0	2·19
10	3·35	29·5	0·63	240	12·0	105·6	2·25
20	5·45	48·0	1·02	1380	12·4	109·5	2·3
45	9·37	82·5	1·75				
Dibromodinitromethane, 0·1173 g.							
2	3·32	15·75	0·34	60	6·63	31·46	0·67
5	4·36	20·69	0·44	120	7·48	35·5	0·75
10	4·73	22·45	0·48	180	8·04	38·2	0·81
20	5·54	26·3	0·56	1140	10·08	47·8	1·02
45	6·34	30·1	0·64				
Potassium dinitromethane, 0·0450 g.							
2	3·5	23·65	0·50	60	5·44	36·75	0·78
5	4·68	31·6	0·67	90	5·66	38·23	0·81
10	4·87	32·9	0·7	150	5·85	39·5	0·84
20	5·1	34·45	0·73	1200	6·94	46·9	1·0
30	5·3	35·7	0·76				

Gases liberated in Thiourea Experiments.—Some of the nitro-compounds studied yield halogen acids as reduction products, and in view of Coade and Werner's results (*loc. cit.*) it seemed of interest to examine the gases liberated in the different reactions. The gas from tetranitromethane is mainly nitrogen; in the other cases examined, the proportion of nitric oxide increases when halogen acid is present in the reaction mixture.

Substance.	Products.	N, %.	NO, %.
Tetranitromethane	$3HNO_2$	93·8	6·2
Chloronitroform	$2HNO_2 + HCl$	87·1	12·9
Bromonitroform	$2HNO_2 + HBr$	83·9	16·1
Dibromodinitromethane	$HNO_2 + 2HBr$	68·6	31·4

Identification of Formamidine Disulphide.—Tetranitromethane (0·9778 g.) in alcohol was slowly added to an aqueous solution of thiourea (4 g.), and the mixture kept for 5 hours. Sulphur, precipitated as a decomposition product of the disulphide, was removed, and an alcoholic solution of picric acid added to the filtrate. The picrate of formamidine disulphide soon separated, m. p. 153°, the amount being about 20% of the theoretical quantity required for reduction of the nitro-compound.

Preparation of Potassium Nitroform.—A solution of glycerol (40 g.) in water (400 c.c.) containing potassium hydroxide (30 g.) is, when cool, treated with tetranitromethane (30 g.), and the mixture mechanically shaken. Yellow crystals of potassium nitroform soon separate, the change being complete in about 30 minutes. The salt is removed and fresh potassium hydroxide, glycerol, and tetranitromethane are added to the filtrate: the yield in this case is greater owing to the solution being initially saturated with potassium nitroform. The salt separates in a fine crystalline state of good purity, and the method has proved to be quite safe [Found: K, 20·55. Calc. for $CK(NO_2)_3$: K, 20·7%].

The approximate solubilities of the salt in water and in alcohol were determined; in the latter case the solvent was carefully evaporated and the dry salt weighed. In the case of aqueous solutions a volume of the saturated solution was drawn off at a definite temperature, acidified with sulphuric acid, and evaporated to dryness, and the potassium estimated as sulphate. The salt is only moderately easily soluble in water at temperatures below 30°, but above that temperature the solubility increases rapidly.

Temp.	0°	10°	20°	30°	40°	50°	60°
Water (g. per litre)	16·7	21·5	28·3	35·9	62·9	111·5	193·8
Alcohol (g. per litre)	1·845		1·976		2·544		5·29

The barium salt may be prepared by a similar method using baryta and glycerol. It separates as a very fine, pale yellow, microcrystalline powder.

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