CC.—*Titanous Salts as Reducing Agents.*

By Edmund Knecht.

In previous communications (*Ber.*, 1903, **36**, 166, 1549; 1904, **37**, 3475; 1905, **38**, 3318; 1907, **40**, 3819; P., 1910, 229; *J. Soc. Dyers and Col.*, 1906, **22**, 165, 330; 1908, **24**, 68; 1909, **25**, 135, 160; 1915, **34**, 94, 205, 241; 1920, **36**, 215; *J. Soc. Chem. Ind.*, 1908, **27**, 434; 1909, **28**, 189; 1915, **34**, 126), it has been shown that the powerful reducing action of the titanous salts can be utilised with advantage in the quantitative determination of a number of inorganic and organic substances by volumetric methods, details of which are described. The present work contains an account of further observations and of some new applications of standardised titanous chloride solution in the volumetric analysis of certain organic compounds.

Reduction of Sulphuric Acid.—If a strong (15 per cent.) solution of titanous sulphate is added slowly to concentrated sulphuric acid, reaction at once ensues; the amethyst colour of the titanous salt disappears and there is copious disengagement of sulphur dioxide. On adding larger amounts of the titanous sulphate solution, the reaction ceases owing to the dilution of the acid; sulphuric acid diluted with its own volume of water no longer reacts with titanous sulphate.

Quantitative Reduction of Nitric to Nitrous Acid.—The reduction of nitric acid to oxides of nitrogen and ammonia (*Ber.*, 1903, **36**, 166), to a stage intermediate between nitric oxide and nitrous oxide ("New Reduction Methods in Volumetric Analysis," p. 5), and quantitatively to ammonia (*J. Soc. Chem. Ind.*, 1915, **34**, 126) has been described.

Further experimental work on the subject, in which I have been ably assisted by Mr. J. H. Platt, has shown that if an acceptor, in the form of a primary aromatic amine, is present in the solution and the ratio $2TiCl_3 : HNO_3$ is adhered to, reduction of the nitric acid to nitrous acid is effected and a quantitative yield of the corresponding diazonium compound results, according to the general equation—

$$Ar{\cdot}NH_2{,}HCl + HNO_3 + 2TiCl_3 + 2HCl = Ar{\cdot}N{:}NCl + 2TiCl_4 + 3H_2O.$$

The nitrates of aniline, *o*- and *p*-toluidines, α-naphthylamine, benzidine, and dianisidine, when thus treated in dilute aqueous solution in presence of hydrochloric acid, gave the corresponding diazonium compounds in quantitative yields. The reaction takes place, under these conditions, rapidly at the ordinary temperature, and in dilute solution no appreciable rise in temperature is apparent.

So far, the reaction has not given good results with the nitrates of the nitro-amines; the nitro-group apparently reacts simultaneously with the reducing agent and this gives rise to complications. The diazotisation of aminoazobenzene by this reaction was likewise unsuccessful. Nitrosodimethylaniline was obtained in only 16 per cent. of the theoretical yield, and *p*-nitrosophenol in amount only sufficient for its identification. On the other hand, β-naphthol, treated with the theoretical amounts of nitric acid and titanous chloride, gave good yields of nitrosonaphthol.

The primary aromatic amines above referred to were diazotised by dissolving a known weight of the pure base in a sufficiency of dilute hydrochloric acid, making the solution approximately *N*/10 with cold water, and adding exactly one equivalent of *N*/10-nitric acid followed, after stirring, by the theoretical amount of titanous chloride (2 equiv.), and stirring for about a minute (compare also Möhlau, D.R.-P. 25146, 1883; O. N. Witt, *Ber.*, 1909, **42**, 2953).

The titration of the resulting diazo-compounds was effected in the usual way, by running the diazo-solution into a freshly prepared standard solution of pure sodium β-naphthoxide in sodium carbonate. In one instance, the result of the ordinary titration was controlled by a titration with titanous chloride (reduction to the diazohydrazide) by Knecht and Thompson's method (*J. Soc. Dyers and Col.*, 1920, **36**, 215), rosinduline being employed as indicator.

In the results stated below, the amount of diazo-compound is given, for the sake of convenience, in terms of the primary amine.

Base.	Gram taken.	Gram found.	Base.	Gram taken.	Gram found.
Aniline	0·1261	0·1264	Benzidine	0·0920	0·0907
,, ...	0·3200	0·3187 (K. & T.)	Dianisidine	0·1322	0·1320
o-Toluidine	0·1548	0·1544	α-Naphthylamine	0·1350	0·1348
p-Toluidine	0·1436	0·1437			

Reduction of the Nitronaphthalenes.—In the titration of α-nitronaphthalene with titanous chloride, it was noticed that when hydrochloric acid was present in excess, the results were liable to come out too low, and it was consequently recommended (*op. cit.*, p. 130) that in carrying out this titration, no acid should be added, a sufficiency being present for the purpose in the standard titanous chloride solution. English (*J. Ind. Eng. Chem.*, 1920, **12**, 994), Callan, Henderson, and Strafford (*J. Soc. Chem. Ind.*, 1920, **39**, 86T), and Callan and Henderson (*ibid.*, 1922, **41**, 157T) have done further work on the titration of nitro-compounds with titanous chloride and Callan and Henderson have suggested the use of titanous sulphate in place of the chloride, all risk of the reaction taking an abnormal course being thereby avoided.

The immediate cause of the low results obtained in titrating with titanous chloride in presence of much hydrochloric acid appeared to be indicated in a paper by Seidler (*Ber.*, 1878, **11**, 1201), who obtained, besides α-naphthylamine, a considerable amount of a monochloronaphthylamine (m. p. 98°) on reducing α-nitronaphthalene with tin and concentrated hydrochloric acid. Although this observation made it probable that titanous chloride in presence of excess hydrochloric acid would effect a similar change, this had not been proved and the reaction has now been tried under various conditions of working and the products examined. It was found that when the amount of hydrochloric acid present was such as to satisfy the equation

$$C_{10}H_7{\cdot}NO_2 + 6TiCl_3 + 7HCl = C_{10}H_7{\cdot}NH_2,HCl + 2H_2O + 6TiCl_4,$$

the titration results were satisfactory. By increasing the acidity to 24HCl, it was found that, after reduction had gone to completion, a considerable amount of unchanged titanous chloride remained in the solution. On cooling, the latter deposited a considerable crop of crystalline plates with a metallic lustre, which were recrystallised twice from water to remove the titanium. The base isolated from these crystals was purified by recrystallisation from alcohol and from water and was ultimately obtained in long, hairy, almost colourless needles melting at 97° and having the composition $C_{10}H_6Cl{\cdot}NH_2$. Titrated with standard potassium bromate, it took up one equivalent of bromine, and it is evident from these data that it is 4-chloro-α-naphthylamine. From the yield obtained, this halogenated naphthylamine would appear to represent, under the conditions chosen, the main product of the reaction.

β-Nitronaphthalene, prepared by Sandmeyer's method (*Ber.*, 1887, **20**, 1407), was reduced under the same conditions, but no chlorination occurred, the resulting base consisting of pure β-naphthylamine. A normal result was also obtained in titrating this nitronaphthalene in presence of a large excess of hydrochloric acid. 1 : 8-Dinitronaphthalene also gave correct results when similarly titrated.

For the preparation of 4-chloro-α-naphthylamine, a solution of 10 grams of α-nitronaphthalene in 20 c.c. of hot alcohol was run slowly into a boiling solution of 278 c.c. of titanous chloride (20 per cent.) and 150 c.c. of concentrated hydrochloric acid, the boiling being continued for 6 minutes. The whole of the nitronaphthalene was reduced and the solution still contained a considerable amount of unchanged titanous chloride. The crystals of the hydrochloride that separated on cooling (11·6 grams), after recrystallising twice from water, were treated in aqueous solution with ammonia in slight excess. The separated base showed m. p. 93°, which is higher than the figure (85—86°) given by Atterberg (*Ber.*, 1887, **10**, 549) for 4-chloro-α-naphthylamine. After repeated recrystallisation from alcohol and from water, it was not found possible to raise the m. p. beyond 97°, whereas that stated by Reverdin (*Ber.*, 1900, **33**, 682) is 98° (Found: Cl = 20·11; *M*, by Rast's method, = 172·2. Calc. for $C_{10}H_8NCl$, Cl = 19·97 per cent.; *M* = 177·5).

The amount of bromine taken up by titration with potassium bromate was 0·0809 gram for 0·1696 gram of the base, which represents slightly more than one equivalent (0·0765 gram) per molecule.

4-Chloro-α-naphthylamine is readily diazotised and the diazo-compound combines completely with β-naphthol in alkaline solution, giving a scarlet, insoluble *azo*-compound, red needles, m. p.

213°, from alcohol (Found: Cl = 10·30. $C_{10}H_6Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$ requires Cl = 10·67 per cent.). Sulphonated with fuming sulphuric acid, the product dyes wool a bright shade of scarlet.

In some further experiments on the effect of hydrochloric acid on the reduction of nitronaphthalene by titanous chloride, it was ascertained that with 12 mols. of hydrochloric acid a product resulted which showed m. p. between 80° and 90°. The highest yield of the monochloro-derivative appeared to be obtained by using 24 mols. of hydrochloric acid and an excess of 5 per cent. of titanous chloride over the 4 mols. required to produce the monochloro-compound. Under these conditions a 94 per cent. yield of crude 4-chloro-α-naphthylamine, m. p. 94°, was obtained.

Titrations.

(In collaboration with Miss E. HIBBERT.)

Tetramethyldiaminobenzhydrol, $OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ (Michler's hydrol).—This compound, although not used as a dyestuff, is of some importance as an intermediate product. Its solution in hydrochloric acid is colourless, but on the addition of excess of sodium tartrate, an intense blue colour at once develops. On titrating this solution with titanous chloride, the amount of the reagent required to decolorise is found to be exactly equivalent to two atoms of hydrogen. On exposing the reduced solution to the air, the blue colour returns immediately. This behaviour is not usual with the paraquinonoid compounds, and calls to mind that of many coloured compounds which are regarded as possessing an orthoquinonoid structure.

Of the phthaleins, only two have so far been titrated by means of titanous chloride, viz., eosin A and rhodamine B. It was considered of interest to add to these two further types and of these gallein and phenolphthalein were chosen. Both these compounds gave on titration the results which would have been expected by theory, *i.e.*, they each required amounts of titanous chloride for decoloration representing 2H. In the case of phenolphthalein, a simple means is thus afforded for the valuation of this drug, whilst in the case of gallein, the titration lends support to the quinonoid structure established by Orndorff and Brewer (*Amer. Chem. J.*, 1900, **23**, 425; 1901, **26**, 97).

Alizarin S.—It has been shown by Bradshaw and A. G. Perkin (J., 1922, **121**, 911) that β-hydroxyanthraquinone behaves abnormally on reduction, whereas anthraquinone itself gave a quantitative yield of anthranol under the same conditions. In these circumstances, it was thought that alizarin S might possibly not behave towards reducing agents in the same way as alizarin, and the titration of this dyestuff was therefore tried. The sodium salt was titrated in presence of sodium tartrate in the same manner as is described for alizarin, flavo- and anthra-purpurin (*J. Soc. Dyers and Col.*, 1915, **34**, 241), and it was found that the solution gave the characteristic intense bluish-green colour * with the first drop of titanous chloride in excess of what would correspond to 4H. Its behaviour on reduction is therefore normal.

Tartrazine.—This dyestuff was prepared in the form of its pure crystallised tripotassium salt. For reduction with titanous chloride in presence of sodium tartrate to the disappearance of the yellow colour, it required the equivalent of 4H.

Isatin.—It is known that an aqueous solution of isatin is readily decolorised by acid reducing agents (Bayer, *Ber.*, 1879, **12**, 1309). The solution, on exposure to air, becomes yellow again, owing to regeneration of the isatin. Using titanous chloride as the reducing agent, it was found that the disappearance of the yellow colour coincided with the formation of dioxindole, according to the equation $C_8H_5O_2N + H_2 = C_8H_7O_2N$. By employing a trace of patent-blue as indicator, the end-point (yellow-green-blue-colourless) is rendered more distinct, especially in artificial light. Rhodamine B also may serve as indicator, but all the other dyestuffs tried for the purpose were reduced before the isatin was affected.

Phenylhydrazine.—Although phenylhydrazine is not acted upon by titanous chloride, it can nevertheless be accurately titrated by means of this reagent using an indirect method. It has been found, namely, that 1 mol. of methylene-blue requires for its reduction to the leuco-compound exactly 1 mol. of phenylhydrazine. The end-point obtained in the direct titration is not sufficiently sharp to ensure that degree of accuracy which is required in volumetric analysis. By adding the phenylhydrazine to an excess of methylene-blue, boiling for about a minute in a current of carbon dioxide, and titrating back the excess with titanous chloride, accurate results have been obtained. Nitrogen is evolved during the reduction (see also Landauer, Inaug. Dissert., Munich, 1909), which evidently takes place in the following sense :

$$C_{16}H_{18}N_3ClS + C_6H_8N_2 = C_6H_6 + C_{16}H_{20}N_3ClS + N_2.$$

Glucosazone.—E. Fischer (*Ber.*, 1886, **19**, 1920) has expressed

---

* Besides being shown by the compounds named, this colour is shown by the α-amino- and hydroxy-anthraquinones, quinizarin, anthrarufin, α-aminoalizarin (alizarin claret), and purpurin, but not by anthraquinone, the β-amino- and hydroxy-anthraquinones, β-nitroalizarin, nor by anthragallol. The colour is instantly destroyed by the addition of a ferric salt.

the view that the reduction of this compound by zinc and acetic acid takes place according to the equation

$$C_{18}H_{22}O_4N_4 + 6H + H_2O = C_6H_{13}O_5N + NH_3 + 2C_6H_5{\cdot}NH_2.$$

It is now found that in carrying out the titration with titanous chloride in presence of sodium tartrate, the amount of hydrogen required is exactly that shown in the above equation. In order to obtain a suitable end-point, it was found convenient to effect the reduction with excess of titanous chloride and to titrate the excess with crystal-scarlet or lanacyl-blue. The reaction has been successfully applied to the quantitative estimation of glucose. It is hoped to give details of the method in a further communication.

Details of Analytical Methods.

Tetramethyldiaminobenzhydrol.—The hydrol (purified by crystallisation from tetralene; m. p. 98°) was dissolved in dilute hydrochloric acid, excess of sodium tartrate added, and titration effected in an atmosphere of carbon dioxide to the disappearance of the blue colour. 0·1042 Gram of substance required 22·0 c.c. of $TiCl_3$ (1 c.c. = 0·001958 gram of Fe), and as 270 grams of the hydrol = 112 grams of iron, the amount present was 99·7 per cent.

Phenolphthalein.—An alcoholic solution is run into water, about 2 c.c. of a saturated solution of sodium tartrate are added, and the titration is then proceeded with as in the case of gallein. The end-point is ascertained by allowing a drop to coalesce on a spot-plate with a drop of caustic soda solution, when it will have ceased to give the characteristic red colour. 0·1005 Gram of phenolphthalein (m. p. 256°) required 20·2 c.c. of $TiCl_3$ (1 c.c. = 0·001755 gram of Fe) and on the basis of 1 mol. of phenolphthalein requiring 2H for its reduction to phenolphthalein this gives 100·1 per cent. Another estimation gave 99·9 per cent.

Gallein.—Since this compound does not show any definite m. p. and it was necessary, in order to verify the accuracy of the method, to have a guarantee of its purity, the tetra-acetyl compound was prepared in the crystallised state from commercial gallein. This showed m. p. 242°, which is in accordance with the figure found by Orndorff and Brewer (*loc. cit.*). From the acetyl compound, the gallein was obtained in a crystallised state by hydrolysing with a small amount of concentrated sulphuric acid, diluting with water, and allowing to stand over-night. The characteristic, well-defined crystals of gallein thus obtained were washed with water and dried. In carrying out the titration, an alcoholic solution of a known weight of gallein was run into 2 c.c. of a saturated solution of sodium tartrate and about 20 c.c. of water, the solution was then warmed at about 50° and titrated with standard titanous chloride, in a current of carbon dioxide, until the magenta colour gave place to a pale yellow. 0·1001 Gram of gallein required 28·7 c.c. of $TiCl_3$ (1 c.c. = 0·001019 gram of Fe) and assuming that 2H have been required for the reduction, this gives gallein 94·93 per cent.; water at 110° 4·77 per cent. (calc. for 1 mol., 4·71): total 99·70 per cent.

Alizarin S.—The titration is effected by adding excess of titanous chloride to a solution of a known weight of the dyestuff in water containing excess of sodium tartrate. The solution is boiled in a current of carbon dioxide, and a measured volume of titanous chloride run in. The excess of the latter is ascertained by back-titration with iron alum to the disappearance of the blue-green coloration. 0·0511 Gram of alizarin S required 15·0 c.c. of $TiCl_3$ (1 c.c. = 0·002112 gram of Fe): colouring matter = 94·6; water at 110° = 5·11 (calc. for 1 mol., 5·0): total = 99·71 per cent.

Sodium as sulphate, in the anhydrous substance = 20·64 (required by theory, 20·76 per cent.).

Tartrazine.—This substance is titrated direct in hydrochloric acid solution and at an elevated temperature, like an ordinary mono-azo-dye. The disappearance of the yellow colour is taken as the end-point. 0·1931 Gram of substance required 23·1 c.c. of $TiCl_3$ (1 c.c. = 0·002771 gram of Fe) and assuming that 582 parts of the dye require 224 of iron, the following result is obtained: tartrazine = 86·11; water at 110° = 13·98 (calc. for $5H_2O$, 13·93): total 100·00 per cent.

The purity of the dyestuff was controlled by an estimation of the potassium (Found: K = 44·67. Calc. for $C_{16}H_9O_9N_4S_2K_3$, K = 44·84 per cent.).

Isatin.—The isatin was crystallised from water and had m. p. 201°. The titration offers no difficulty, reduction to the colourless dioxindole taking place at the ordinary temperature in a current of carbon dioxide and without any additions. 0·04347 Gram of substance in 50 c.c. of water required 36·3 c.c. of $TiCl_3$ (1 c.c. = 0·001016 gram of Fe), denoting 99·82 per cent. purity.

With patent-blue as indicator, the same sample gave 99·8 per cent. Although of no value as a dyestuff, isatin is employed in considerable amounts in the manufacture of certain indigoid vat dyes.

Estimation of Phenylhydrazine.—Phenylhydrazine (0·3320 gram) was dissolved in hydrochloric acid and made up to 100 c.c. and to 10 c.c. of the solution 50 c.c. of methylene-blue (1 c.c. = 0·001244 gram of Fe) were added. The solution was boiled in a current of carbon dioxide, and the excess of methylene-blue titrated with titanous chloride (1 c.c. = 0·001275 gram of Fe) of which 26·7 c.c. were required. Since 108 of phenylhydrazine = 122 of Fe, the amount present was 98·8 per cent. An estimation carried out in a similar way on a phenylhydrazine from a different source gave 99·3 per cent., whilst Kahlbaum's product taken fresh from a sealed vessel gave 99·8 per cent.

In consequence of the facility with which phenylhydrazine can be estimated by the above method, an attempt was made to determine the phenylhydrazine in the products of acid hydrolysis of a known weight of glucosazone. To this end, 0·322 gram of glucosazone was warmed with concentrated hydrochloric acid and the resulting product made up to 100 c.c. To 10 c.c. of this solution, 50 c.c. of methylene-blue (1 c.c. = 0·001244 gram of Fe) were added, the mixture was heated to boiling in a current of carbon dioxide, and the excess of methylene-blue titrated back with titanous chloride (1 c.c. of $TiCl_3$ = 0·001275 gram of Fe), of which 15·7 c.c. were required. Since 216 of phenylhydrazine are formed from 358 of glucosazone, the result, expressed in terms of the latter, represents 99·75 per cent.

Reduction of Phenylglucosazone.—To a solution of 0·02915 gram of glucosazone in alcohol, 2 c.c. of a saturated solution of sodium tartrate were added and 50 c.c. of titanous chloride were run in. After the mixture had boiled in an atmosphere of carbon dioxide for 6 minutes, excess of hydrochloric acid was added and the excess of titanous chloride titrated back with crystal-scarlet. This showed 34·2 c.c. excess $TiCl_3$. 15·8 C.c. of $TiCl_3$ (1 c.c. = 0·001736 gram of Fe) had therefore been consumed in the reduction, and assuming 358 of glucosazone to be equivalent to 336 of Fe (6H), this gives 99·85 per cent. 0·0694 Gram of glucosazone, treated as above with 50 c.c. $TiCl_3$ (1 c.c. = 0·001712 gram of Fe) and the excess afterwards estimated with crystal-scarlet, showed 12·1 c.c. excess; that is, 37·9 c.c. were used by the glucosazone, which is equivalent to 99·6 per cent.

In another experiment, 0·02550 gram of glucosazone, reduced in the same way and back-titrated with lanacyl-blue, used up 8·6 c.c. of $TiCl_3$ (1 c.c. = 0·002771 gram of Fe), which represents 0·02538 gram, or 99·5 per cent. of glucosazone.

Summary.

It is shown that, under chosen conditions, titanous chloride reduces nitric acid quantitatively to nitrous acid. The reaction may be employed as a convenient means for diazotising primary aromatic amines.

By reducing α-nitronaphthalene with titanous chloride in pres-

ence of a large excess of hydrochloric acid, the principal product of the reaction (about 94 per cent.) is 4-chloro-α-naphthylamine.

Methods are described for the volumetric estimation of tetramethyldiaminobenzhydrol, phenolphthalein, gallein, alizarin S, tartrazine, isatin, glucosazone, and phenylhydrazine. The last-named substance may also be accurately estimated in the products of the acid hydrolysis of glucosazone.

MUNICIPAL COLLEGE OF TECHNOLOGY,
MANCHESTER UNIVERSITY.

[*Received, April* 9*th,* 1924.]