**571.** *Some Oxidation–Reduction Reactions of Hydroxylamine.*

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Evidence is presented for the intermediate formation of the NH_2 radical in the reduction of hydroxylamine in acid, aqueous solution. This radical is able to initiate the polymerisation of vinyl monomers and to attack various aromatic substrates. A preliminary investigation of the products formed by the attack by NH_2 radicals on benzene has been made.

The overall energetics of the primary reaction between reducing agent and hydroxylamine are discussed, with reference to the observed formation of the NH_2 radical rather than the OH radical.

HYDROXYLAMINE in acid solution is reduced by strong reducing agents to ammonia and water (see, *e.g.*, Stähler, *Ber.*, 1904, **37**, 4732; Kurtenacker and Werner, *Z. anorg. Chem.*, 1927, **160**, 333) :

$$2Cr^{++} + HO \cdot NH_3^+ + 2H^+ \longrightarrow 2Cr^{+++} + NH_4^+ + H_2O$$
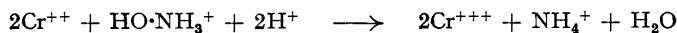
The formal similarity between this reaction and the reduction of hydrogen peroxide by ferrous ions, which under suitable conditions obeys the stoicheiometric equation :

$$2Fe^{++} + HO \cdot OH + 2H^+ \longrightarrow 2Fe^{+++} + H_2O + H_2O$$
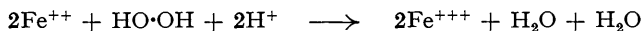
has prompted an investigation of the detailed mechanism of the reactions of hydroxylamine by using methods similar to those employed in the elucidation of the mechanism of the hydrogen peroxide–ferrous reaction (Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155). In the latter case it has been established that the reaction takes place in two steps, each involving the oxidation of a ferrous ion to the ferric state, and the intermediate formation of the OH radical. This was shown by allowing substrate molecules (monomers such as methyl methacrylate) to compete with the ferrous ions for the OH radicals produced in the first stage of the reaction, thus causing a drop in the $[Fe^{++}]/[H_2O_2]$ consumption fraction from 2 in the absence of substrate, to 1 in high substrate concentrations.

In the reduction of hydroxylamine in the presence of substrate (X), there are two extreme possibilities, *viz.* :

1   (*a*) $M^{n+} + HO \cdot NH_3^+ \longrightarrow M^{(n+1)+} + (H^+ + NH_2^-) + OH^-$

      (*b*) $M^{n+} + OH \longrightarrow M^{(n+1)+} + OH^-$

      (*c*) $OH + X \longrightarrow X \cdot OH$

2   (*a*) $M^{n+} + HO \cdot NH_3^+ \longrightarrow M^{(n+1)+} + NH_2 + (OH^- + H^+)$

      (*b*) $M^{n+} + NH_2 \longrightarrow M^{(n+1)+} + NH_2^-$

      (*c*) $X + NH_2 \longrightarrow XNH_2$

The overall reaction may involve the intermediate formation of OH radicals or of NH_2 radicals or possibly both. The main aim of this investigation has been the attempt to decide whether the NH_2 radical, which does not appear to have been reported previously as an intermediate in reactions in aqueous solution, is produced in this system.

EXPERIMENTAL.

Cylinder nitrogen was partially freed from oxygen by passage through columns containing a solution of sodium dithionite, sodium hydroxide, and sodium anthraquinone-β-sulphonate. The gas was

finally purified by passage through a tower of finely divided copper on kieselguhr at 220° (Meyer and Ronge, *Angew. Chem.*, 1939, **52**, 637). This oxygen-free gas was used in all cases where de-aeration of solutions was necessary.

Hydroxylamine hydrochloride was of " AnalaR " quality. Hydroxylamine sulphate was a B.D.H. product and was recrystallised once from water. Titanium(III) sulphate and titanium(III) chloride solutions were obtained from Messrs. Peter Spence, and were found to contain 0·070 and 0·018 mole of the corresponding ferrous salt, respectively, per mole of titanous salt. Iron-free titanium(III) chloride was prepared by the electrolytic reduction of a solution of pure titanium(IV) chloride in M-hydrochloric acid, at a lead cathode. In the experiments described, however, the presence of small quantities of ferrous ion proved to be unimportant.

Solutions of chromium(II), vanadium(II), and molybdenum(III) sulphates * were prepared by the zinc-amalgam reduction of solutions of chromium(III) sulphate, vanadium(IV) sulphate, and molybdic acid (all " AnalaR "), respectively, in N-sulphuric acid.

Methyl methacrylate was obtained from Imperial Chemical Industries Limited, and was freed from stabilisers with potassium hydroxide solution followed by vacuum distillation under nitrogen. Acrylonitrile was obtained from L. Light & Co. and was purified by fractional distillation under nitrogen. Other reagents were of B.D.H. " AnalaR " quality.

In the preliminary experiments, measured quantities of solutions of the reducing agent were added to solutions of hydroxylamine sulphate, previously de-aerated by passage of oxygen-free nitrogen, in the presence of methyl methacrylate or of acrylonitrile. The solutions were kept under an atmosphere of nitrogen. The concentrations of reducing agent and of hydroxylamine sulphate were of the order 10^{-3}M.—2×10^{-2}M. and the sulphuric acid concentration 10^{-2}—2N. Monomer concentrations were 0·05M. in the case of methyl methacrylate and 1M. in the case of acrylonitrile.

Under these conditions titanium(III) was oxidised rapidly, and almost immediate formation of visible polymer occurred. In similarly dilute acid solutions chromium(II), vanadium(II), and molybdenum(III) were slowly oxidised, and visible polymer appeared only after about ten minutes. With iron(II) (in 10^{-2}N-sulphuric acid) several days elapsed before the appearance of polymer; after a month, a considerable amount of polymer had been formed, though tests on the solution showed no iron(III). It is, however, known that in acid solution iron(III) is reduced fairly rapidly to iron(II) by hydroxylamine (Mitchell, *J.*, 1926, 336). The use of iron(II) in the presence of acetate ion and of fluoride ion at pH $\rightleftharpoons$ 5 caused a considerable decrease in the time of appearance of polymer, but even so the reaction appeared to be very slow. Ferrocyanide in acid, neutral, and alkaline solution gave no trace of polymer after several weeks. In all the above cases parallel experiments, carried out in the absence of reducing agent or of hydroxylamine, showed no evidence of polymer formation.

The production of polymer is strong evidence for the formation, as reaction intermediates, of radicals able to attack the double bond of a vinyl monomer, and hence is evidence in favour of the two-stage nature of the overall reaction.

In more detailed experiments on the stoicheiometry of the reaction in the presence of substrates, titanium(III) was used as the reducing ion, as in this case comparatively short reaction times could be achieved. Moreover the reaction between titanium(III) and hydroxylamine is known to be stoicheiometric under the appropriate conditions, and can be used for the quantitative determination of hydroxylamine (Stähler, *loc. cit.*; Bray, Simpson, and MacKenzie, *J. Amer. Chem. Soc.*, 1919, **41**, 1363).

These experiments were carried out by adding about a 20% excess of standard titanium(III) chloride solution to previously de-aerated solutions of hydroxylamine hydrochloride and methyl methacrylate. The mixture was well stirred in an atmosphere of nitrogen for 30 minutes, and then the excess of titanium(III) chloride was titrated against standard cerium(IV) sulphate solution, *N*-phenylanthranilic acid being used as indicator. The mixture was then made alkaline with sodium hydroxide solution, and ammonia determined by the Kjeldahl method. Blank experiments were done in the absence of hydroxylamine; the blank correction was reproducible and equivalent to 2% of the ammonia produced in the absence of monomer. The time of addition of the titanium(III) chloride solution from a micro-burette was in all cases approximately 90 seconds; check experiments in which the time of addition was varied between 30 seconds and 8 minutes showed that within this range the rate of addition had no detectable effect on the stoicheiometry. Under the conditions of the experiments the half life of the reaction was of the order of 2 minutes, so that 30 minutes was an ample allowance for complete reaction. The experiments were done mainly at room temperature (20° $\pm$ 1°); a few experiments at 10° and 30° gave results identical within the experimental error.

Fig. 1 shows the dependence of the consumption fraction $[Ti^{3+}]/[HO\cdot NH_3^+]$ on monomer concentration; Fig. 2 shows the dependence of $[NH_3]_{evolved}/[HO\cdot NH_3^+]_{consumed}$ on monomer concentration, in the same set of experiments; while Fig. 3 shows $[Ti^{3+}]/[HO\cdot NH_3^+]$ plotted against $[NH_3]_{evolved}/[HO\cdot NH_3^+]_{consumed}$. The concentration of methyl methacrylate varied from zero to a 2M-emulsion; $[HO\cdot NH_3^+] = 5 \times 10^{-3}$M., $[HCl] = 0\cdot6$N.

Reference to equations 1*a*, *b*, and *c* and 2*a*, *b*, and *c* shows that only if the primary reaction is 2*a* exclusively can the experimental finding (Fig. 3)

$$[Ti^{3+}]_{consumed}/[HO\cdot NH_3^+]_{consumed} = 1 + \{[NH_3]_{consumed}/[HO\cdot NH_3^+]_{consumed}\}$$

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* The possible complexes formed by these ions in solution have not been specified since we are dealing only with the overall stoicheiometry and not with the detailed mechanism.

be satisfied. The other extreme, involving the exclusive production of the OH radical, would lead to a constant $[NH_3]_{evolved}/[HO \cdot NH_3^+]_{consumed}$ of unity, independently of value of $[Ti^{3+}]_{consumed}/[HO \cdot NH_3^+]_{consumed}$. It thus appears that the NH_2 radical is an intermediate in the reduction of hydroxylamine, and that it is an effective initiator of polymerisation. The weight-average molecular weight of the polymer as determined by viscosity experiments varied between 40,000 and 300,000. Determination of the nitrogen content of the polymers was not attempted.
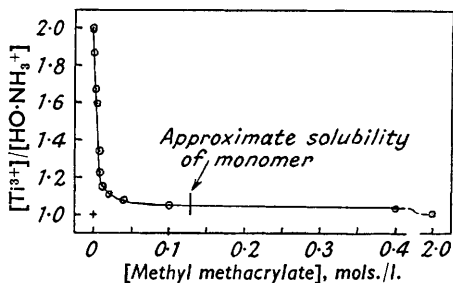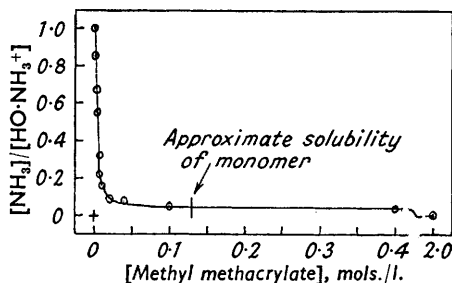
FIG. 1.

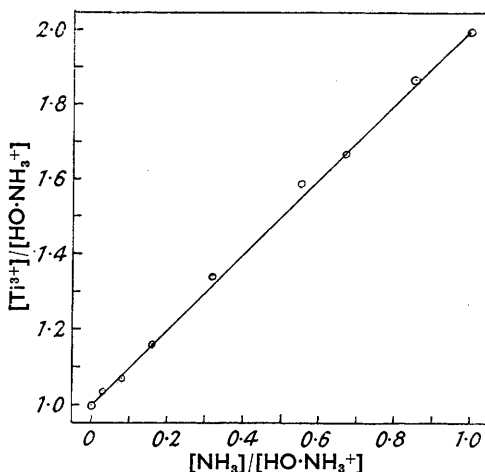[Methyl methacrylate], mols./l.

FIG. 2.

[Methyl methacrylate], mols./l.

FIG. 3.

$[NH_3]/[HO \cdot NH_3^+]$

FIG. 4.

[Benzene], mols./l.

Initial $[HO \cdot NH_3^+] = 4 \times 10^{-3}$M.

FIG. 5.

[Benzene], mols./l.

Initial $[HO \cdot NH_3^+] = 10^{-2}$M.

FIG. 6.
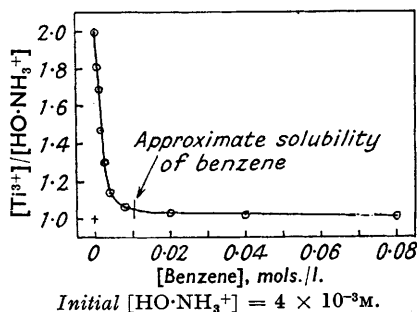

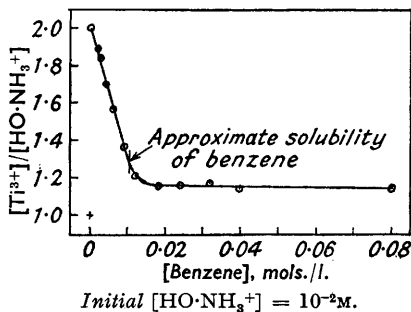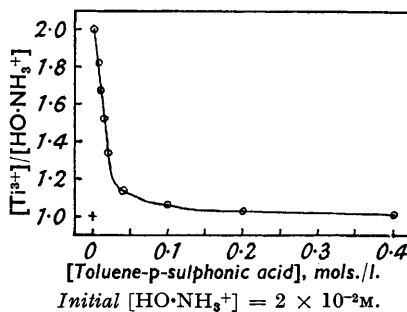[Toluene-p-sulphonic acid], mols./l.

Initial $[HO \cdot NH_3^+] = 2 \times 10^{-2}$M.

Substrates other than methyl methacrylate were also used, and Figs. 4 and 5 show the consumption fraction $[Ti^{3+}]/[HO \cdot NH_3^+]$ plotted against benzene concentration. In Fig. 4 the acid was 0·6N-hydrochloric acid; $[HO \cdot NH_3^+] = 4 \times 10^{-3}$M.; in Fig. 5 titanium(III) sulphate was used, the acid was 0·4N-sulphuric acid and $[HO \cdot NH_3^+] = 10^{-2}$M. Fig. 6 shows the consumption fraction plotted against toluene-*p*-sulphonic acid concentration. Here the total acid strength was maintained at 0·4N. in each experiment by the addition of the appropriate amount of sulphuric acid; $[HO \cdot NH_3^+]$ was 0·02M.

The table shows the consumption fraction for 0·02M-hydroxylamine in 0·5N-sulphuric acid in the presence of 0·1M-solutions of various substrates.

Substrate.		Pyridinium ion.	Toluene (emulsion).	Benzene (emulsion).	Benzoic acid (heterogeneous).	Naphthalene-2-sulphonic acid.	Toluene-*p*-sulphonic acid.	Benzenesulphonic acid.
Consumption fraction [Ti³⁺]/[HO·NH₃⁺] ...		2·0	1·98	1·33	1·24	1·17	1·12	1·07	1·04
Fraction of NH₂ radicals reacting with the substrate		0	0·02	0·67	0·76	0·83	0·88	0·93	0·96

The use of aromatic sulphonic acids may thus prove advantageous in studies of this kind, where the use of monomer is inconvenient because of the high concentrations often needed and the heavy precipitate of polymer produced. It is noteworthy that apparently the pyridinium ion does not react with the NH_2 radicals produced.

Products Formed by the Reaction of NH_2 *Radicals and Benzene.*—A few preliminary experiments have been made to determine the products formed by the titanium(III)–hydroxylamine reaction in the presence of benzene.

Nitrogen was bubbled for 30 minutes through sulphuric acid (500 ml.; N.) and benzene (100 ml.) contained in a 2-litre flask. De-aerated, approximately M-solutions of titanium(III) sulphate and hydroxylamine sulphate were run in simultaneously with vigorous stirring; about 50—100 ml. of each solution were used, and the time of addition was 30—60 minutes. The addition was so controlled that the hydroxylamine was always in slight excess until the end of the addition, when the titanium solution was added in slight excess, which was then removed by addition of a small amount of ferric iron.

The benzene layer was then separated, and the solution extracted twice with ether (250 ml.). The benzene, and the ether extracts, were dried (Na_2SO_4) and evaporated. No trace of any product was found in these extracts, nor was the characteristic odour of diphenyl noticeable after evaporation of the solvents. Test experiments showed that diphenyl can be recovered almost quantitatively on evaporation of a dilute solution in benzene.

The aqueous mixture was then cooled in an ice-bath and made alkaline with a slight excess of potassium hydroxide solution. A gelatinous precipitate of hydrated titania resulted. It proved impossible to filter this off and so the mixture was extracted with ether (500 ml.), and the ethereal extract was extracted with hydrochloric acid (20 ml.; 2N.) followed by water (10 ml.). The ether was then used for a further extraction of the aqueous mixture, and the process repeated eight times. The combined acid and water extract (about 250 ml.) should contain any amines produced in the reaction, as the corresponding hydrochlorides. Evaporation of part of the solution gave, on cooling, diphenyl, m. p. and mixed m. p. 69°. The remainder of the solution was made alkaline, extracted with ether, and the ether evaporated. About 0·5 ml. of dark brown oil remained, and this gave a positive test for nitrogen. Alcoholic potassium hydroxide and chloroform gave the characteristic odour of an organic *iso*cyanide; diazotisation and coupling of the salt with β-naphthol gave a red precipitate which slowly decomposed to a brown oil; attempts to prepare a benzoyl derivative and a picrate gave tarry products. It seems probable, therefore, that the brown oil contained an aromatic amine, though no aniline could be detected.

Qualitative experiments showed that if, after separation of the benzene layer and ether extracts, the acid aqueous reaction mixture was boiled diphenyl was formed in fairly large amounts. Accordingly a quantitative experiment was done in which the acid reaction mixture, obtained as previously described, was refluxed for 6 hours and the diphenyl formed then steam-distilled. The total diphenyl obtained was approximately 0·12 g.-mol. (*i.e.*, equivalent to 0·24 g.-radical of NH_2) while the amounts of hydroxylamine and titanium(III) used in the experiment (consumption fraction [Ti³⁺]/[HO·NH₃⁺] = 1·2) showed that approximately 2·4 g.-radicals of NH_2 had attacked the benzene substrate.

As no trace of diphenyl was found in either the benzene layer or the ethereal extracts of the cold acid reaction mixture, it seems probable that the reaction between an NH_2 radical and a benzene molecule in aqueous solution does not lead to the formation of phenyl radicals and ammonia, *viz.*,

$$NH_2 + H·C_6H_5 \longrightarrow NH_3 + C_6H_5·$$
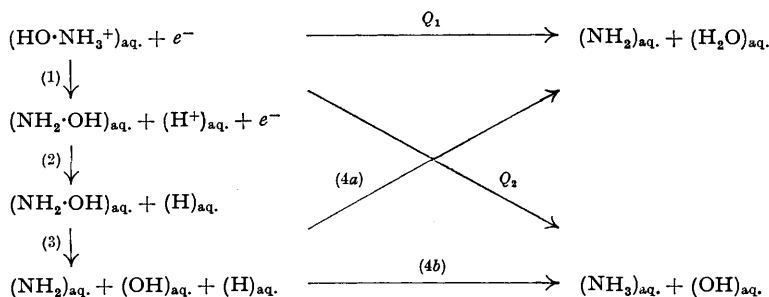$$(2C_6H_5· \longrightarrow C_6H_5·C_6H_5)$$
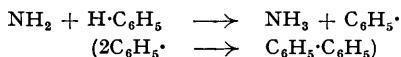
Consistently with the experimental observations, it is suggested that the primary product of attack of NH_2 radicals on benzene is the addition compound $C_6H_6·NH_2$, and that a proportion of these radicals dimerise to give a di(amino*cyclo*hexadienyl); such compounds do not appear to have been recorded in the literature. It seems likely, however, that boiling in acid solution could cause loss of ammonia with the formation of diphenyl. As the total diphenyl production was only of the order of 10% of the amount to be expected if all the NH_2 radicals which reacted with the benzene had led to diphenyl formation, a major proportion of $C_6H_6·NH_2$ radicals, rather than dimerising, must undergo other reactions, possibly addition of NH_2 or even oxidation by the NH_2 radical.

DISCUSSION OF THE ENERGETICS OF THE PRIMARY REACTION.

The experimental results show that the first step in the reduction of hydroxylamine in acid solution results almost completely, possibly exclusively, in the formation of NH_2 radicals; a

consideration of the relevant energy proves of interest. From the following cycles, the influence of these factors on the overall energy change of reaction can be seen :

$$(HO \cdot NH_3^+)_{aq.} + e^- \xrightarrow{\quad Q_1 \quad} (NH_2)_{aq.} + (H_2O)_{aq.}$$

$$(1) \downarrow$$

$$(NH_2 \cdot OH)_{aq.} + (H^+)_{aq.} + e^-$$

$$(2) \downarrow$$

$$(NH_2 \cdot OH)_{aq.} + (H)_{aq.}$$

$$(3) \downarrow \qquad (4a) \qquad Q_2$$

$$(NH_2)_{aq.} + (OH)_{aq.} + (H)_{aq.} \xrightarrow[\quad (4b) \quad]{} (NH_3)_{aq.} + (OH)_{aq.}$$

It thus appears that the difference of heats of reactions involving the formation of NH_2 or of OH radicals, *i.e.* $(Q_1 - Q_2)$, is determined solely by the terms :

$$D_{HO-H}^{aq.} - D_{NH_2-H}^{aq.} = D_{HO-H}^{gas} + (S_{H_2O}^{aq.} - S_{OH}^{aq.}) - D_{NH_2-H}^{gas} - (S_{NH_3}^{aq.} - S_{NH_2}^{aq.})$$

where D's are bond dissociation energies and S's are solution energies.

We suggest that the second and the fourth term in the above equation are small and roughly equal, *i.e.*,

$$(S_{H_2O}^{aq.} - S_{OH}^{aq.}) \sim (S_{NH_3}^{aq.} - S_{NH_2}^{aq.})$$

There are no direct evaluations of the heats of solution of the free radicals OH and NH_2, but we can obtain an idea of the magnitude of these terms from considerations of the heats of solution of hydrogen peroxide, water, hydrazine, and ammonia :

Molecule.	H_2O_2.	H_2O.	N_2H_4.	NH_3.
Heat of solution in water, kcals./mole	12	10·5	14	8·5

The heat of dissociation of hydrogen peroxide into two OH radicals in water does not differ appreciably from the dissociation heat in the gas phase, suggesting that $S_{H_2O_2}^{aq.} = 2S_{OH}^{aq.}$. Such considerations support the assumption made above, and hence we suggest that

$$Q_1 - Q_2 = D_{HO-H}^{gas} - D_{NH_2-H}^{gas}$$

The recent values of 118 and of 104 kcals./mole for the bond dissociation energy of HO–H (Dwyers and Oldenburg, *J. Chem. Phys.*, 1944, **12**, 351) and of NH_2–H (Szwarc, *J. Chem. Phys.*, 1949, **17**, 505), respectively, being used, the overall heat of the primary reaction is calculated to be at least 12·5 kcals. more exothermic in the case where NH_2 radicals are produced than with the alternative OH-radical production, and this difference can be ascribed mainly to the greater heat of formation of the H–OH bond compared with the NH_2–H bond. The qualitative parallelism which exists for simple primary steps between the rates and the overall energy changes of similar reactions may be expected to apply in this case, and thus the experimental finding of exclusive NH_2-radical production may be understood.

It is important to notice that these conclusions hold whether $NH_2 \cdot OH \cdot H^+$ or $NH_2 \cdot OH$ is the reacting species, as up to 4 (*a*, *b*) the steps in the energy cycle are identical.

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