OXIDATION STUDIES—VII

Oxidation of Hydrazine Sulphate and Hydroxylamine by Cobalt (III)

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ABSTRACT

Kinetics of oxidation of hydrazine sulphate and hydroxylamine by Co^{3+} in nitric and sulphuric acid media at 10–15° C. were studied. In H_2SO_4 medium, kinetic evidence was obtained for complex formation between Co^{3+}-Substrate for both substrates whereas no such evidence was found in HNO_3 medium. The effects of $[H^+]$, μ, $[HSO_4^-]$, $[SO_4^-]$, $[Co^{2+}]$ and temperature on the reaction rates were studied. An inverse dependence of the rates on $[H^+]$ was noticed in both media with both substrates but decreasing effect of $[HSO_4^-]$ was observed only with NH_2OH in H_2SO_4 medium. Conclusions were drawn as to the nature of the active species: In H_2SO_4 medium for hydrazine sulphate, Co^{3+} (aq.) was concluded to be the active species; similarly for NH_2OH, $CoOH^{2+}$ was the active species. In HNO_3 medium for both substrates $CoOH^{2+}$ was the active oxidant. Nitrogen and Ammonia were found to be the products of oxidation with both substrates in both media. Stoichiometries were established and suitable mechanisms were proposed. The rate laws were formulated and the various equilibria and rate constants were evaluated.

INTRODUCTION

KINETICS of oxidation of hydrazine (or hydrazine-sulphate) by various metal ions such as Fe^{3+},[1,5] Ce^{4+},[2,3,6] V^{5+},[2] Ti^{3+},[2] Ag^+,[7] Cu^{2+},[8] Mo^{6+},[9] and metal oxides such as PbO_2 and Pb_3O_4[10] and MnO_2[11] have been reported in detail. Both one and two electron transfer mechanisms have been suggested depending on the products of oxidation. The earlier work on oxidation of hydrazine in aqueous solution by a variety of oxidants has been reviewed by Higginson.[12] With hydroxylamine, however, comparatively little data are available. Oxidations by Ce^{4+},[13] Cu^{2+},[14] peroxydisulphate[15] and Ti^{3+},[15a, b] have been reported and possible mechanisms discussed. We have studied oxidation of hydrazine sulphate and

hydroxylamine (H.A.) by CO^{3+} in aqueous nitric and sulphuric acid media and in the light of our experimental results possible mechanisms have been discussed in this paper.

Experimental

Hydrazine sulphate (B.D.H., A.R.) and hydroxylamine sulphate (E. Merck, G.R.) were used without further purification. Cobaltic sulphate and nitrate were prepared as described earlier.[1] Other reagents such as sodium nitrate, bisulphates of sodium or potassium, potassium iodide, sodium thiosulphate, sulphuric acid, nitric acid, potassium iodate, sodium bromate, sodium bromide, etc., were all of analar grade. Water distilled over alkaline $KMnO_4$ and deionized over Bioderminrolit mixed bed ion exchange resin (permutit; U.K.) was used for preparation of reagent and kinetic runs.

Experiments were conducted in $6'' \times 1''$ pyrex tubes using a large Dewar flask as a thermostat. Concentrations of Co^{3+} (initial and during the experiments) were determined by addition of excess potassium iodide to Co^{3+} solutions and immediate titration of the liberated iodine with standard thiosulphate. Under the experimental conditions used, the direct reaction between iodine and hydrazine sulphate (or hydroxylamine) was extremely slow which facilitated this method of estimating Co^{3+}. Cerimetry in conjunction with Fe^{2+} could not be used for Co^{3+} since hydrazine sulphate and H.A. reacted with Ce^{4+} instantaneously.

Results and Discussion

In the temperature range 0–10°C. $[Co^{3+}]$ = 1·25 × 10^{-3} M and $[H^+]$ = 0·4–2·0 M, oxidation of hydrazine sulphate – H.A. under identical conditions. Both substrates were rapidly oxidised in nitric acid while oxidations were comparatively slow (especially with hydrazine sulphate) in H_2SO_4 medium. Spontaneous reduction of Co^{3+} by water was very insignificant under the experimental conditions.

(i) *Individual orders.*—The order of $[Co^{3+}]$ for rate of disappearance of the latter, $-R_{co}$, was found to be unity in H_2SO_4 and HNO_3 media for oxidations of both the substrates, viz., plots of $\log a/a$ x vs. time were linear upto 90% conversion of Co^{3+} and also plots of (R_{co}) vs. $[Co^{3+}]$ were linear (Fig. 1, A, B, C, D). The pseudounimolecular rate constants, k', sec.$^{-1}$ were directly proportional to [Substrate] in both media which indicated the order w.r.t. the latter was also unity. Plots of k', sec.$^{-1}$ vs. [Substrate] were devoid of intercepts in HNO_3 medium (Fig. 2, A and Fig. 3, A) which

showed the absence of any complex formation or any side reaction. However, in H_2SO_4 medium for both substrates, k', sec.$^{-1}$ values could be fitted into Michaelis-Menten reciprocal plots (Fig. 2, B, C, D, E and Fig. 3, B, C, D, E) indicating possible formation of complexes, Co^{3+} — Hydrazine sulphate and Co^{3+} — Hydroxylamine in H_2SO_4 medium.
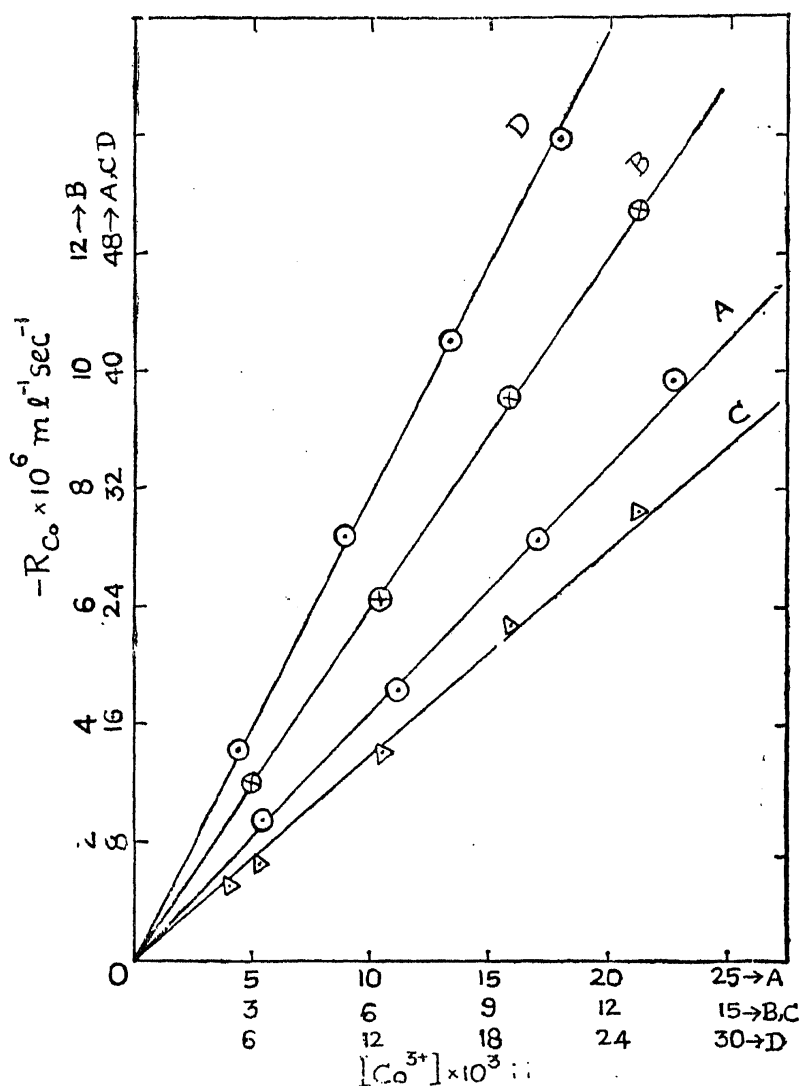

FIG. 1. Variation of $- R_{Co}$ with substrate at [substrate] $= 28 \times 10^{-3}$ M. and temp.: 5° C.
A: N_2H_4, [HNO_3] $= 1\cdot3$ M, $\mu = 1\cdot5$ M; B N_2H_4, [H_2SO_4] $= 2\cdot0$ M, $\mu = 2\cdot1$ M; C NH_2OH, [H_2SO_4] $= 2\cdot0$ M, $\mu = 2\cdot1$ M; (D) NH_2OH, [HNO_3] $= 2\cdot0$ M, $\mu = 2\cdot2$ M.

(ii) *Effect of* [H^+].—An inverse dependence of the rates on [H^+] was observed with both substrates in HNO_3 as well as H_2SO_4 media (*cf.* Fig. 4, plots A and B) which indicated that in the latter medium, $CoOH^{2+}$ was probably the active species. However, in H_2SO_4 medium, when the slopes of $1/k'$, *vs.* 1/[Substrate] plots at different [H^+] were plotted against [H^+] no intercept on the ordinate was obtained with hydrazine sulphate (Fig. 4, C)

while an intercept was obtained in the case of H.A. (Fig. 4, D). Occurrence of acid dependent reaction alone with hydrazine sulphate while acid-dependent as well as acid-independent reactions with H.A. was therefore obvious. The acid dependent reaction may be due to (i) equilibria for complex formation involving $[H^+]$ or (ii) the active species for oxidation being $CoOH$; $CoSO_4^+$, etc., or due to both (i) and (ii). Further insight into the nature of the reaction in H_2SO_4 medium was obtained by studying the effect of $[SO_4^=]$ and $[HSO_4^-]$ on the reaction rates. The acid-independent reaction is evidently due to complex formation between Co^3 and unprotonated H.A.
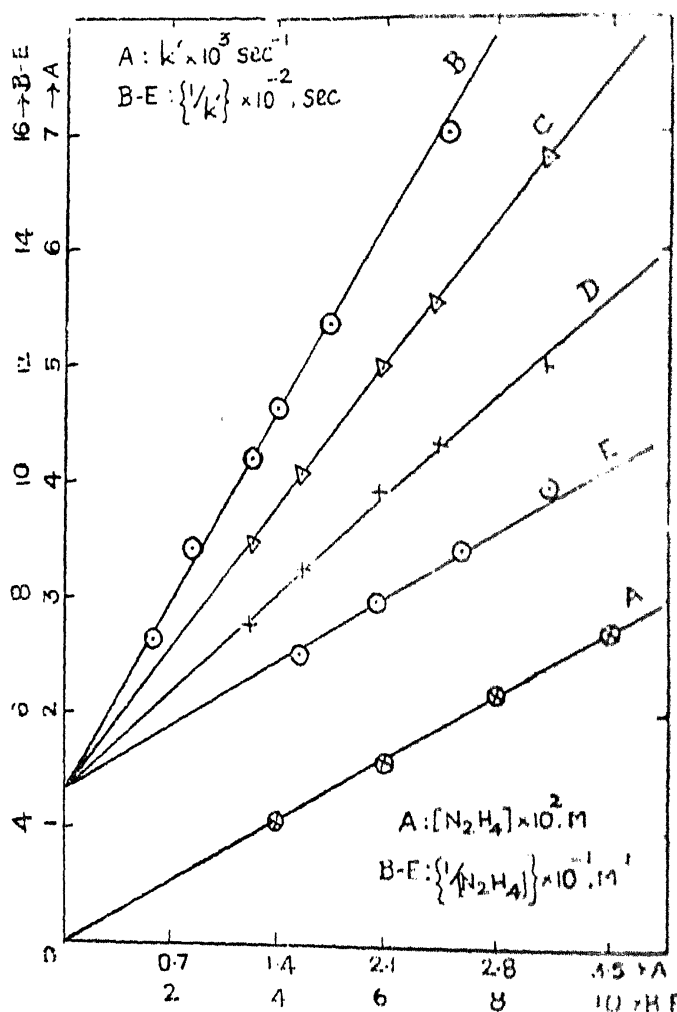

FIG. 2. Variation of k', sec.$^{-1}$ with $[N_2H_4]$ at temp.: 5° C.; μ 2·1 M A $[HNO_3]$ = 1·0 M, $[CO^3]$ = 2·537 × 10^{-3} M; B, C, D, E: $[H_2SO_4]$ 2·0 M, 1·5 M, 1·0 M and 0·7 M respectively and $[CC^{3+}]$ = (2·5–3) × 10^{-3} M.

(iii) *Effect of* $[HSO_4^-]$ *and* $[SO_4^=]$.—Both substrates were unaffected by $[SO_4^=]$ at constant μ. With increasing $[HSO_4^-]$ at constant μ, the rates of oxidation of hydrazine sulphate was also unaffected which showed that

only $Co^{3+}{}_{(aq)}$ was probably the active species and the observed dependence of [H⁺] on the rates was due to complex formation between hydrazinium ion, $N_2H_5^+$ and Co^3. With H.A. the decreasing rates [40°, decrease for variation of (HSO_4) from 0·5 to 2·0 M] with increasing $[HSO_4]$ at constant μ excluded the possibility of $CoSO_4$ being the active species and at the same time indicated that possibly $CoOH^{2+}$ was also the active species in addition to $Co^{3+}{}_{(aq)}$. In H_2SO_4 medium, the observed rate constant must increase
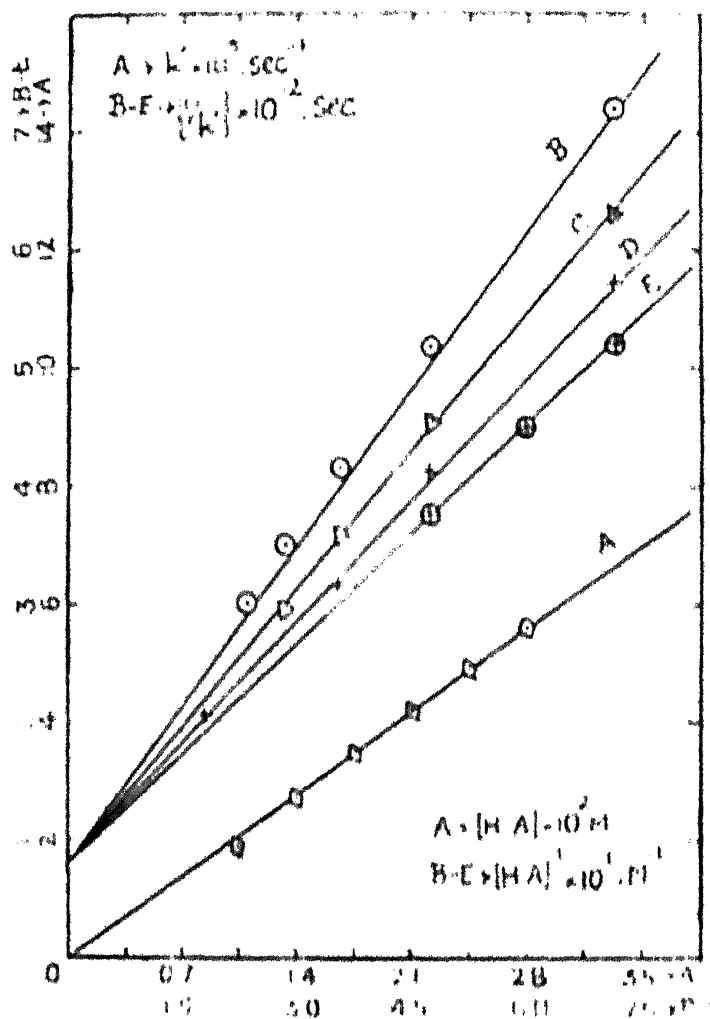

Fig. 3. Variation of k', sec⁻¹ with [NH₂OH] at temp.: 5 C.; μ ~ 2·1 M. A: [HNO₃] ~ 1·0 M, [Co³⁺] ~ 3·422 × 10⁻³ M; (B, C, D, E) [H₂SO₄] ~ 2·0 M, 1·5 M, 1·0 M and 0·7 M respectively and [Co³⁺] ~ (2–3) × 10⁻³ M.

with increasing (HSO_4^-) if $CoSO_4^+$ were the active species and decrease with increasing $[HSO_4^-]$ if $CoOH^{2+}$ were the active species while for both $CoOH^{2+}$ and $CoSO_4^+$ as active species, inverse dependence of the rates on [H⁺] would be obtained.[18]

$$(Co^{3+} + H_2O \rightleftharpoons CoOH^{2+} + H^+; \quad Co^{3+} + HSO_4^- \rightleftharpoons CoSO_4^+ + H^+),$$
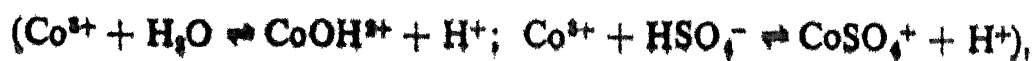
Since the Michaelis-Menten reciprocal plots at different [H⁺] (Figs. 3 and 4) converge to the same point, it is also clear that the complexes Co^{2+} — H.A. and $CoOH^{2+}$ — H.A. must have the stabilities of the same magnitude and may decompose at the same rate to give products.
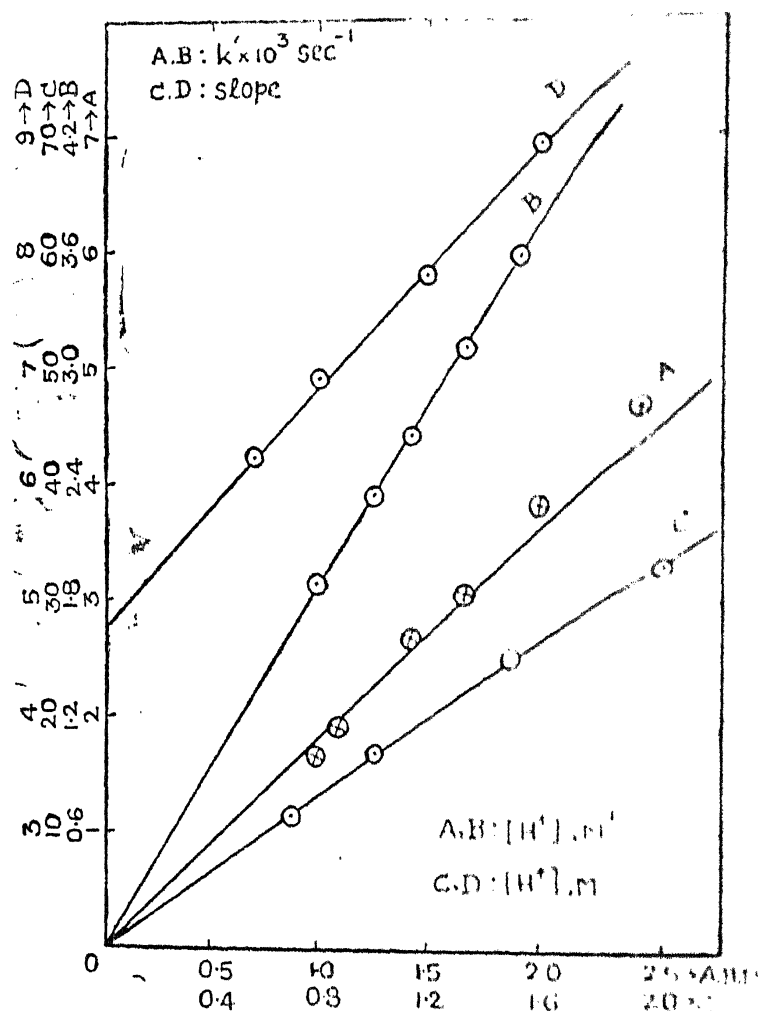

Fig. 4. Variation of k', sec.$^{-1}$ and slope with [H⁺]. A: $[N_2H_4]$ — 21 · 10⁻³ M, $(Co^{2+}$ = (2·5–3·5) × 10⁻³ M, [HNO₃] medium; B: [NH₂OH] 10·5 × 10⁻³ M, $[Co^{2+}]$ × 10⁻³ M, HNO₃ medium; C and D: H₂SO₄ medium; C: slope vs. [H⁺] with N₂H₄ and D: slope vs. [H⁺] with NH₂OH.

(iv) *Effect of* μ.—The reaction rates decreased with increasing μ in both media with both substrates (for a 4-fold increase in μ, rates decreased by Ca 15% in HNO₃ and by 30% in H₂SO₄), probably due to the effect of μ on the various complex equilibria involved.

(v) *Effect of* Co^{2+}.—Reaction rates were unaffected by [Co²⁺] in HNO₃ medium while in H₂SO₄ medium the rates were almost doubled. Probably
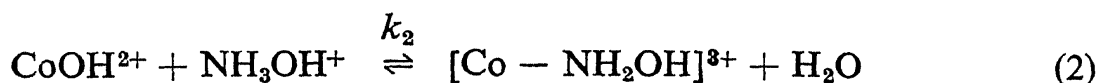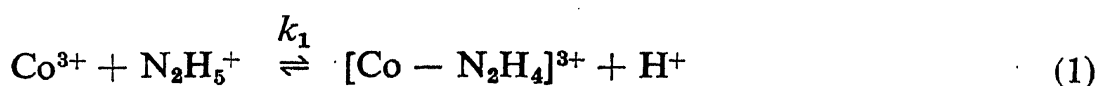
Co^2-hydrazine sulphate (or HA) complex[19–21] + Co^{3+} reaction takes precedence over the dissociation of the complex, Co^{3+}-substrate.

(vi) *Product analysis and stoichiometry.*—On adding Co^{3+} to the substrate, nitrogen was evolved very rapidly in HNO_3 medium and less rapidly in H_2SO_4 medium. Ammonia was identified as the other product with both substrates by means of Nessler's reagent from solutions in which Co^{3+} was taken in large excess so as to ensure complete oxidation of the substrates. The test for NH_3 was more positive in H_2SO_4 medium than in HNO_3 medium. Stoichiometries were established under conditions of [Substrate] > Co^{3+}. After completion of the reaction, the solutions were neutralised and then unreacted hydrazine sulphate, and H.A. were estimated with standard potassium iodate and bromate-bromide respectively. Stoichiometries,
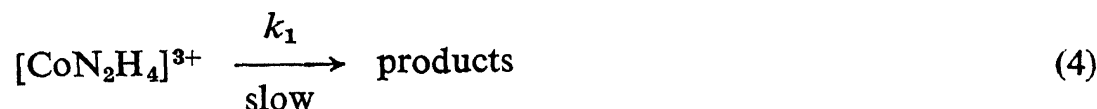
$$\frac{\triangle [Co^{3+}]}{\triangle [H.A.]} = 1\text{--}1 \cdot 4$$

(on the basis of equivalents of Co^{3+}) in H_2SO_4 and $1 \cdot 6$–$2 \cdot 0$ in HNO_3 medium were obtained for Co^{3+}-hydrazine sulphate. With H.A., the stoichiometries were $1 \cdot 6$–2 and 1–$1 \cdot 4$ in H_2SO_4 and HNO_3 media respectively.

(vii) *Mechanism and rate laws.*—Kinetic results indicate that in H_2SO_4 medium, the following rapid reversible complex equilibria are probably involved. Hydrazine sulphate is assumed to dissociate to give $N_2H_5^+$; protonated hydroxylamine, NH_3OH^+ is also assumed to be involved:

$$Co^{3+} + N_2H_5^+ \overset{k_1}{\rightleftharpoons} [Co - N_2H_4]^{3+} + H^+ \tag{1}$$

$$CoOH^{2+} + NH_3OH^+ \overset{k_2}{\rightleftharpoons} [Co - NH_2OH]^{3+} + H_2O \tag{2}$$

$$Co^{3+} + NH_2OH \overset{k_3}{\rightleftharpoons} [Co - NH_2OH]^{3+}. \tag{3}$$

Complexes, then, decompose at a slow rate to yield the products.

$$[CoN_2H_4]^{3+} \xrightarrow[\text{slow}]{k_1} \text{products} \tag{4}$$

$$[CoNH_2OH]^{3+} \xrightarrow[\text{slow}]{k_2} \text{products,} \tag{5}$$

Under conditions of rapid reversible equilibrium and from equations (1 and 4), it follows that

$$[CoN_2H_4]^{3+} = \frac{[Co^{3+}]_{Total}\, K_1\, [N_2H_5^+]}{([H^+] + K_1\, [N_2H_5^+])}$$

$$-R_{Co} = k'\,[Co^{3+}]_T = \frac{k_1\, K_1\, [Co^{3+}]_T\, [N_2H_5^+]}{([H^+] + K_1\, [N_2H_5^+])}$$
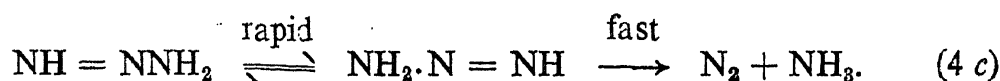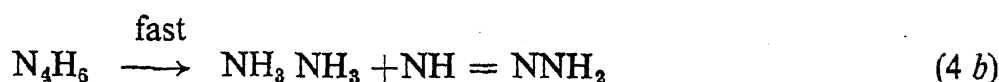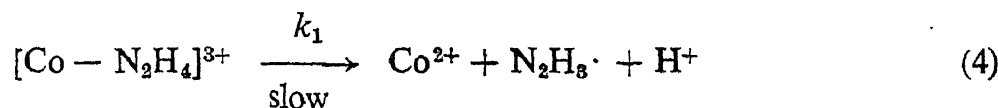
$$\frac{1}{k'} = \frac{1}{k_1} + \frac{[H^+]}{k_1 K_1\, [N_2H_5^+]} \tag{6}$$

where k' is the pseudounimolecular rate constant. Similar expressions can be derived for H.A. also [from equations (3) and (5)] involving K_2 and K_3 instead of K_1 and without any (H^+) term.

The decomposition of the complexes leading to products probably occurs as follows:

Case 1 (*a*)

Hydrazine sulphate in H_2SO_4.—

$$[Co - N_2H_4]^{3+} \xrightarrow[\text{slow}]{k_1} Co^{2+} + N_2H_3\cdot + H^+ \tag{4}$$

$$2\,N_2H_3\cdot \xrightarrow{\text{fast}} N_4H_6 \tag{4 a}$$

$$N_4H_6 \xrightarrow{\text{fast}} NH_3\,NH_3 + NH = NNH_2 \tag{4 b}$$

$$NH = NNH_2 \underset{\text{rapid}}{\rightleftharpoons} NH_2\cdot N = NH \xrightarrow{\text{fast}} N_2 + NH_3. \tag{4 c}$$
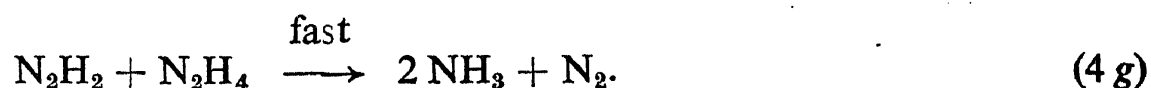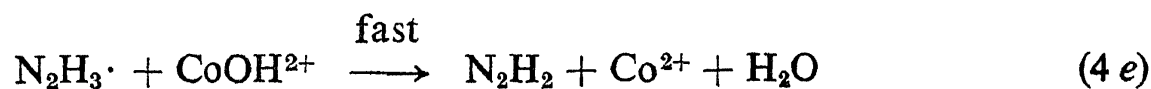
This scheme explains our experimental results and the observed stoichiometry. The above reaction sequence was assumed for oxidation of hydrazine sulphate by Fe^{3+},[2–5] Ce^{4+} [2, 3] and Mn^{3+} [3]. The slight variation in stoichiometry is probably due to $N_2H_3\cdot$ reacting to some extent with another Co^{3+} leading to products.

Case 1 (*b*)

Hydrazine sulphate in HNO_3.—The observed stoichiometry indicates that in HNO_3 medium, probably N_2H_3 undergoes further oxidation to N_2H_2

which then undergoes a series fast reactions leading to products (*cf.* oxidation of hydrazine sulphate by Fe^{3+} [2-5] and Ferric ethylene diamine tetraacetate).[2] The following steps are probably involved with $CoOH^{2+}$ as the active entity inferred from kinetics.

$$N_2H_5^+ + CoOH^{2+} \xrightarrow[\text{slow } via \text{ transition complex}]{k_3} N_2H_3\cdot + Co^{2+} + H_2O$$

$$(4\,d)$$

$$N_2H_3\cdot + CoOH^{2+} \xrightarrow{\text{fast}} N_2H_2 + Co^{2+} + H_2O \qquad (4\,e)$$

$$2\,N_2H_2 \xrightarrow{\text{fast}} N_2H_4 + N_2 \qquad (4\,f)$$

$$N_2H_2 + N_2H_4 \xrightarrow{\text{fast}} 2\,NH_3 + N_2. \qquad (4\,g)$$
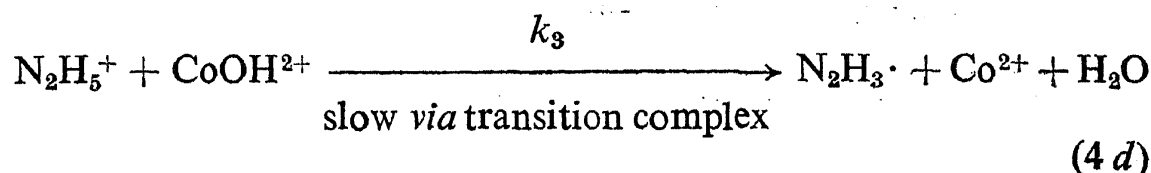
According to the reaction steps suggested, the rate laws for oxidation of hydrazine sulphate are as follows:

$$-R_{co} = \frac{k_1 K_1 [Co^{3+}] [N_2H_5^+]}{[H^+] + K_1 [N_2H_5^+]} \text{ in } H_2SO_4 \text{ medium} \qquad (7)$$

$$-R_{co} = k_3 [CoOH^{2+}] [N_2H_5^+] = \frac{k_3' [Co^{3+}] [N_2H_4]}{[H^+]}$$

$$\text{in } HNO_3 \text{ medium} \qquad (8)$$

where $k_3' = k_3$, K_4 and $K_4 =$ Hydrolytic equilibrium constant for the formation of $CoOH^{2+}$.

Case 2 (a)

NH₂OH in H₂SO₄.—Assuming the true stoichiometry to be 1:1, the oxidation mechanism is probably the following (*cf.* oxidation by Ce^{4+} [3]):

$$[Co-NH_2OH]^{3+} \xrightarrow[\text{slow}]{k_2} Co^{2+} + NH_2O\cdot + H^+ \qquad (5)$$

$$2\,NH_2O\cdot \xrightarrow{\text{fast}} N_2 + 2\,H_2O. \qquad (5\,a)$$
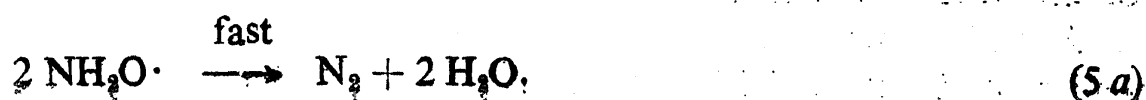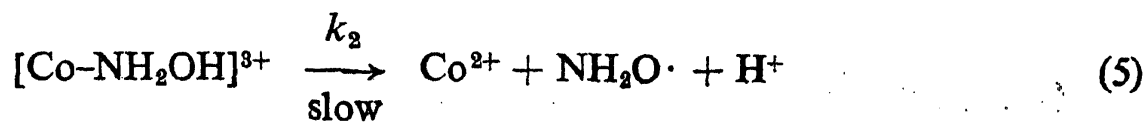
The formation of NH_3 may be due to the occurrence of further reaction of the type:

$$NH_2O\cdot + Co^{3+} \longrightarrow Co^{2+} + HNO + H^+ \qquad (5\,b)$$

$$HNO\cdot + NH_2O\cdot \longrightarrow NH_3 + \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \qquad (5\,c)$$
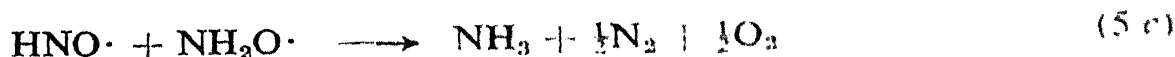
This is also consistent with the varying stoichiometry of the reaction.

Case 2 (b)

NH_2OH in HNO_3.—The reaction steps are probably the same as under 2 (a) except the first step may involve direct interaction between H.A. and $CoOH^{2+}$ without any complex formation [cf. equation. (2)]:

$$CoOH^{2+} + NH_3OH^+ \xrightarrow[\text{slow}]{k_4}$$

$$Co^{2+} + NH_2O\cdot + H_2O + H^+. \qquad (9)$$
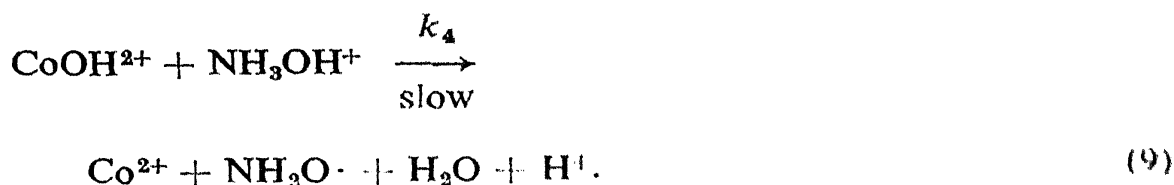
In HNO_3 medium steps (9) and (5 a) appear to be predominant and this is in conformity with the stoichiometry varying between 1–1·4 and also the less positive test for NH_3. In H_2SO_4 medium on the other hand steps (5 b) and (5 c) appear to occur to a greater extent. However, these conclusions are only inferential based on the kinetic data alone. The rate laws for $-R_{co}$ follow from the above mechanism as:

$$-R_{co} = k_4 [CoOH^{2+}] [H.A.] = \frac{k_4' [Co^{3+}] [H.A.]}{[H^+]}$$

$$\text{in } HNO_3 \text{ medium} \qquad (10)$$

where

$$k_4' = k_4 K_4$$

$$-R_{co} = \frac{k_2 K_2 [Co^{3+}] [H.A.]}{[H^+] + K_2 [H.A.]} + \frac{k_2 K_3 [Co^{3+}][H.A.]}{1 + K_3 [H.A.]}$$

$$\text{in } H_2SO_4 \text{ medium} \qquad (11)$$

(viii) *Evaluation of rate constants: H_2SO_4 medium.*—From intercepts of the Michaelis-Menten reciprocal plots (Figs. 3 and 4, plots B-E), values of k_1 and k_2 were evaluated (cf. equation 6). When the slope of these plots were plotted against $[H^+]$ (Fig. 4, C and D) the slopes of these latter plots

yielded values of K_1 and K_2 (assuming k_1 and k_2) while intercept of such a plot for H.A. (Fig. 4, D) yielded K_3. In HNO_3 medium, the second order rate constants k_3' and k_4' were evaluated from k' vs. [Substrate] as well as k' vs. $1/[H^+]$ plots and found to be in good agreement within the limits of experimental error (Table 1).

TABLE I

Rate and equilibrium constants

	Rate constants		Equilibrium constants	
Substrate	HNO_3 k_3' (or k_4') $\times 10^2$ l.m.$^{-1}$ sec.$^{-1}$	H_2SO_4 k_1' (or k_2') 10^3 sec.$^{-1}$		K (H_2SO_4)
Hydrazine	8·02 (5 C.)	2·17 (5° C.)	K_1	27·6 (5°C.)
sulphate	17·79 (10 C.)	5·0 (10 C.)		54·55 (10°C.)
Hydroxylamine	20·0 (5°C.)	12·5 (5 C.)	K_2	38·62 (5 C.)
	43·3 (10°C.)	25·0 (10 C.)	K_3	16·66 (5° C.)

Various rate and equilibrium parameters are subject to $\pm 6\%$ error since graphical extrapolations have been used for their evaluation.

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