In the other region, the weak and broad band at 2760 cm^{-1} due to the OH bond of HTTA disappears completely in the spectra of the metallic chelates.

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The silver (II) oxide–hydrazine reaction

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In weakly acidic or alkaline conditions, the reaction between silver (II) oxide and hydrazine can be described by the equation

$$2AgO + N_2H_4 \rightarrow 2Ag + N_2 + 2H_2O$$

A kinetic study has shown that this reaction proceeds in two distinct stages. The first stage is the reduction of the silver (II) oxide to silver (I) oxide. In the second stage the silver (I) species is reduced to metallic silver.

The only other example of a heterogeneous oxidation reaction in which two stages can be clearly distinguished involves the addition of manganese or lead dioxides to an iodide salt dissolved in concentrated hydrochloric acid. In this case, the iodide ions are oxidized completely to iodine before any of the latter is transformed into an I^+ species.(1)

EXPERIMENTAL AND RESULTS

Reagents

Silver (II) oxide was prepared by the method of Hammer and Kleinberg.(2) Analysis based on the volume of oxygen liberated in acid solutions indicated a purity of 97 per cent. Hydrazine solutions were prepared daily from AR hydrazine hydrogen sulphate crystals. The pH was adjusted by adding sodium hydroxide, the solutions being kept cool to avoid the reaction with dissolved oxygen which occurs at elevated temperatures.

Buffer solutions.

Buffering in the pH range 3·5–6 was obtained by adding sodium acetate to the hydrazinium salt solutions. Excess hydrazinium salt acted as the buffer in the pH range 7–9·5.

Procedure

50-ml aliquots of 0·1 M hydrazine solution (0·5 M in sodium acetate) were pipetted into a water jacketed reaction flask fitted with a side arm and a three-way stopcock. The stopcock connected the reaction vessel with a water jacketed 10-ml gas burette which was used to measure the volume of nitrogen evolved. The solution was stirred by a magnetic stirrer and the temperature in the system was controlled by circulating water from a thermostatically controlled bath. Milligram quantities of silver (II) oxide were weighed into a small sample boat which was placed in the flask side arm. This arm was sealed by an enclosed magnetic pusher rod. This rod was used to push the solid into the solution when the whole apparatus had reached thermal equilibrium. The volume of gas evolved was

(1) G. J. Moody and J. D. R. Thomas, *J. inorg. nucl. Chem.* **25**, 221 (1963).
(2) R. N. Hammer and J. Kleinberg, *Inorg. Synth.* **4**, 12 (1953).

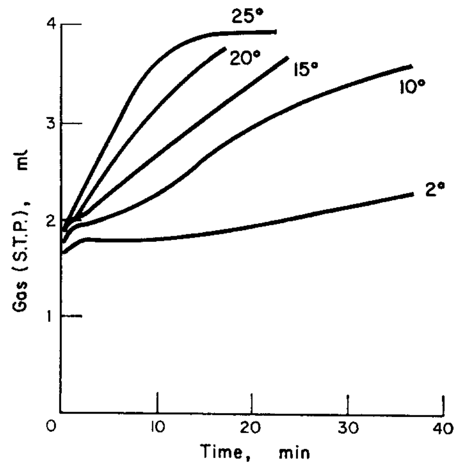

Fig. 1.—The effect of temperature on the reduction of 43 mg AgO by 0·1 M $N_2H_5 \cdot HSO_4$ solution at pH 5·7.

recorded at suitable time intervals from this point. Rate curves obtained using different experimental conditions are shown in Figs. 1 and 2.

At 4°C, there is no apparent reaction at pH 4·5 while at pH > 8 reduction of the oxide to silver is extremely fast. At intermediate pH values, exactly half the theoretical maximum yield of nitrogen was evolved "instantaneously", the solution at this stage remaining black with suspended matter. This initial reaction was too fast to be examined in detail by the technique being used. The second stage of the reaction followed the pattern observed in the silver (I) oxide–hydrazine system which has recently been studied in detail.(8) The mid-point plateau visible on some of the rate curves corresponds to the induction period known to occur in this reaction. For a given set of conditions, the rate of this second stage was several times faster than the value obtained in the silver (I) study; the greater

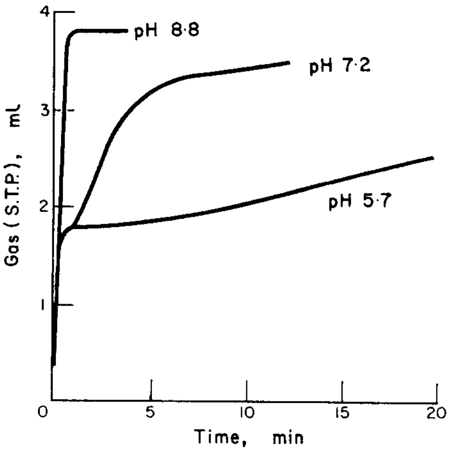

Fig. 2.—The effect of pH on the reduction of 43 mg AgO by 0·1 M $N_2H_5 \cdot HSO_4$ solution at 4°C.

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(8) R. J. Hodges and W. F. Pickering, *Aust. J. Chem.* **19**, 981 (1966).

activity of the oxide formed *in situ* is attributed partly to size effects and partly to the absence of the carbonate impurities which have been shown to be present in air dried silver (I) oxide.⁽⁴⁾

DISCUSSION

The film of Ag_2O formed during the initial reaction must be porous and non-adherent, otherwise this stage of the reaction could not proceed so rapidly to completion. The opposite effect has been observed in a study of the manganese dioxide–ammoniacal hydrazine reaction, where reduction is restricted to a surface layer.⁽⁵⁾

The reaction is believed to involve the intermediate formation of di-imine, i.e.

$$Ag(I){-}O{-}Ag(III) = O + N_2H_4 \rightarrow Ag(I){-}O{-}Ag(I) + H_2O + N_2H_2$$

$$Ag(I){-}O{-}Ag(III) = O + N_2H_2 \rightarrow Ag(I){-}O{-}Ag(I) + H_2O + N_2$$

or,

$$2N_2H_2 \rightarrow N_2 + N_2H_4$$

The reduction of silver (I) species by hydrazine is considered⁽⁸⁾ to proceed via the intermediate formation of $AgN_2H_4^+$ which dissociates to give metallic silver, a proton and N_2H_3. Di-imine may then be formed by collision of the N_2H_3 radical with either Ag^+ or another N_2H_3. This reaction is catalysed by the film of silver formed on the walls of the vessel.

Other sources and secondary reactions of di-imine are described in a recent review.⁽⁶⁾

It is probable that hydrazine is formed as an intermediate in the oxidation of ammonia solutions by silver (II) oxide. However, in the ammonia reaction metallic silver is not produced since the stability of the silver diammine ion is sufficient to inhibit the reduction of the silver (I) formed in the initial reaction. The rate of reduction of silver (I) species by hydrazine is directly related to the concentration of free silver ions and hydrazine, and in ammonia solutions both these values are extremely small. Given sufficient time (e.g. days) decomposition of the ammoniacal silver (I) solutions does occur and it can be suggested that the $AgO{-}NH_3$ system is another reaction which proceeds in two distinct stages. In this case the rate of the second stage is a small fraction of the rate of the first stage.

On adding AgO to ammonia solutions the rate of nitrogen formation has been found⁽⁷⁾ to vary with $[NH_3]^{0.5}$, and as an imide, $=NH$, has been postulated as an intermediate in the catalytic oxidation of ammonia, the first steps in the reaction could be

$$Ag(I){-}O{-}Ag(III) = O + NH_3 \rightarrow Ag_2O + H_2O + NH$$

$$NH + NH_{3(ads)} \rightleftharpoons N_2H_4$$

$$Ag_2O + 4NH_3 + H_2O \rightleftharpoons 2Ag(NH_3)_2OH \rightleftharpoons 2Ag^+ + 4NH_3 + 2OH^-$$

As the concentration of ammonia in solution is reduced, however, the NH radical tends to react with the oxide surface rather than with adsorbed ammonia and increased amounts of nitrite and nitrate ions are produced.

$$Ag(I){-}O{-}Ag(III) = O + NH \rightarrow Ag_2O + HNO$$

$$HNO \xrightarrow{[O]} HNO_2 \xrightarrow{[O]} HNO_3$$

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⁽⁵⁾ C. Drotschmann, *Batterien* **15,** 239 (1961).

⁽⁶⁾ S. Hünig, H. R. Müller and W. Thier, *Angew. Chem.* **4,** 271 (1965).

⁽⁷⁾ W. F. Pickering, *Aust. J. Chem.* **16,** 969 (1963); *ibid.* **17,** 731 (1964).