

and not distributed throughout the mass, and may be thought to be due to the reaction, $2\text{CO} = \text{C} + \text{CO}_2$, a reaction which was probably catalyzed at the zinc surfaces in a manner similar to the catalysis of the same reaction at an iron surface, and which tends to go to the right under the experimental conditions. The rate of this reaction was, however, markedly slower than the reduction of zinc oxide by carbon monoxide. It was customary to observe a decrease of about 30 cc. of carbon monoxide of a total volume of 300 cc. in a number of cycles of passage requiring about ten hours' time whereas, starting with pure carbon dioxide, the content of dioxide was decreased to less than 5% in one hour's time. The rate of carbon formation is, therefore, approximately $1/100$ of the primary reaction investigated, and this is of about the same magnitude as the accidental errors of manipulation and analysis.

We regard the values of heat of reaction and of standard free energy obtained in the present work to be probably correct to within 300 calories.

Summary

Equilibrium data have been obtained for the reaction $\text{ZnO}(\text{s}) + \text{CO} = \text{Zn}(\text{g}) + \text{CO}_2$, over the temperature range 500° to 850° .

A probable error in the older determinations of the heat of formation of zinc oxide is indicated, and a recalculation of thermal data is made which brings the new value in accord with the present work.

Standard free-energy equations are derived for the reduction of zinc oxide by carbon monoxide, and the entropy and free energy of zinc oxide at 25° are calculated.

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THE CATALYTIC EFFECT OF SILVER AMMONIA ION IN THE OXIDATION OF AMMONIA BY PEROXYSULFATES

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Introduction

In a former paper² there were presented the results of an investigation on the rate of the oxidation of chromic salts by peroxysulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), under the influence of silver ion acting as catalyst. The results showed that the rate of the catalyzed reaction is directly proportional to the concentrations both of peroxysulfate ion and silver ion, but independent of the concentration of chromic and hydrogen ions. These facts clearly

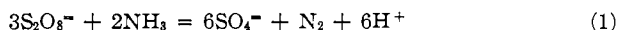
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² Yost, *THIS JOURNAL*, **48**, 152 (1926).

indicated that the slow measurable reaction is that between peroxysulfate ion and silver ion, giving rise to an active intermediate compound. It was also shown that the intermediate compound is a salt of trivalent silver. It seems probable that essentially the same mechanism applies to all oxidation reactions involving peroxysulfates which require silver salts to catalyze them. Marshall³ found that peroxysulfates oxidize ammonia to nitrogen in the presence of silver salts. He made only one rough quantitative experiment on the rate of the reaction, the results of which indicated that it was directly proportional to the concentration of peroxysulfate.

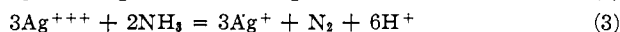
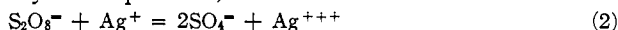
In the present paper the results of an investigation of the ammonia reaction are presented together with a comparison of them with those obtained with the chromium reaction.

The main reaction under consideration is



There is no tendency for the reverse reaction to take place, namely, for the nitrogen to react with sulfuric acid to give peroxysulfates and ammonia. The reaction as written no doubt takes place with a large decrease in free energy. Notwithstanding this, the reaction is a very slow one unless some catalyst is present. Such cases are by no means rare, the example of hydrogen and oxygen at ordinary temperatures having become classical for reactions involving the same conditions.

This oxidation in the presence of silver ion, like that of trivalent chromium, doubtless takes place in two stages, the univalent silver being first oxidized to trivalent silver by the peroxysulfate, and the trivalent silver being then reduced to univalent silver by the ammonia. This mechanism might be indicated by the equations,



The situation is, however, complicated by the fact that the silver ion exists almost wholly in the form of ammonia complexes. Thus it is well established⁴ that the principal ion present in an ammoniacal solution of a silver salt is $Ag(NH_3)_2^+$, or a hydrated form of it. The fact that $Ag(NH_3)_3Cl$ exists as a solid phase⁵ indicates the probable presence also of $Ag(NH_3)_3^+$, at any rate in small amounts. Other ions of a still more complex nature may also be present, though probably in very small proportion. Now the nature of the groups attached to the silver may well have a marked effect on the rate with which the ion reacts with peroxysulfate ion. The results of the present work, compared with those obtained in the previous research, make possible a study of these unique effects.

I wish to acknowledge my appreciation of the advice and criticisms

³ Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900).

⁴ Bodländer and Fittig, *Z. physik. Chem.*, **39**, 597 (1902).

⁵ Isambert, *Compt. rend.*, **66**, 1259 (1868).

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Method of Analysis

A simple and accurate volumetric method of analysis was adopted. The reaction mixture consisted of peroxy sulfate ion, ammonia, silver ammonia ion and potassium hydroxide. When this mixture is acidified, the silver ammonia complex is destroyed and the resulting silver ion may be precipitated by the addition of chloride ion, the reaction being effectively stopped by this procedure. The remaining peroxy sulfate may then be quantitatively reduced to sulfate by ferrous iron. These facts were made the basis of the analytical method adopted, which was as follows. A 25cc. sample of the reaction mixture was withdrawn with a pipet and run into 10 cc. of standard ferrous sulfate solution which contained a few drops of 6 *N* hydrochloric acid and was 1 *N* in sulfuric acid. The resulting mixture was heated to 60°, and after the addition of 50 cc. of water the excess of ferrous iron was titrated with standard permanganate solution. The permanganate was about 0.1 *N* and was standardized against sodium oxalate from the Bureau of Standards.

This method is known to give accurate and uniform results. It is evident that it makes possible the calculation of the concentration of peroxy sulfate in any solution.

Preparation of the Solutions

Potassium Peroxy sulfate and Ammonium Peroxy sulfate.—The c. p. salts were dissolved in redistilled water and made up to a strength of about 0.1 *M*. The solutions were standardized by means of ferrous iron and permanganate.

Silver Perchlorate.—Freshly precipitated silver carbonate was thoroughly washed with water and dissolved in a slight excess of 1 *N* perchloric acid. After filtration, the resulting solution was diluted with redistilled water. The solution was standardized gravimetrically.

Ammonia.—The concentrated solutions were diluted with redistilled water. The stock solutions were standardized by adding a definite volume to a known excess of standard hydrochloric acid and titrating the excess with sodium hydroxide, using methyl red as an indicator.

Potassium Hydroxide.—The c. p. sticks were dissolved in redistilled water, and the resulting solution was filtered and diluted to the desired strength.

Description of the Rate Measurements

A few preliminary experiments established the fact that the catalyzed ammonia reaction was more rapid than the chromium reaction. For this reason it was necessary to use lower concentrations of peroxy sulfate ion than for the latter reaction. With the concentrations used, the reaction was practically complete after a period of two hours.

All the measurements were made at 25°.

The stock solutions and water were mixed by means of pipets. The

silver perchlorate solution was added last, and the time was counted from the moment of its addition. The peroxysulfate, ammonia and potassium hydroxide solutions were first mixed in a 500cc. Florence flask, and this was then placed in the thermostat. After allowing sufficient time for the mixture to come to the temperature, the silver solution was added from the stock solution, which was kept in the thermostat.

Results of the Reaction Rate Measurements

In Table I are given the detailed results of two experiments in which ammonium peroxysulfate was used. In the first column is given the time elapsed in minutes; in the second, the corresponding concentration of peroxysulfate, expressed in millimoles per liter of solution and in the third, the values of the reaction-rate constant calculated (with the concentrations expressed in molalities, not millimolalities) under the assumption that the rate is proportional to the concentrations of peroxysulfate and of total silver present, the significance of which will be discussed later.

TABLE I

RATE EXPERIMENTS WITH AMMONIUM PEROXYSULFATE

Initial millimolal concentrations					
(NH ₄) ₂ S ₂ O ₈ , 13.8; NH ₃ , 68.7; AgClO ₄ , 5.9.			(NH ₄) ₂ S ₂ O ₈ , 13.8; NH ₃ , 112.3; AgClO ₄ , 5.9		
Time	S ₂ O ₈ ⁻ concn.	Rate const.	Time	S ₂ O ₈ ⁻ concn.	Rate const.
0	13.8	..	0	13.8	..
5.5	11.3	6.12	5	10.8	8.31
15.5	8.1	5.81	17	6.4	7.66
26	5.6	5.92	26	4.2	7.75
40	3.7	5.58	39.5	2.4	7.49
57	2.2	5.46	57.5	1.2	7.20
91	0.9	5.08	91	0.4	6.59
125	0.4	4.80	125	0.2	5.73

In Table II are given the detailed results of two typical experiments which were made using potassium peroxysulfate with potassium hydroxide added.

TABLE II

TYPICAL REACTION-RATE EXPERIMENTS WITH POTASSIUM PEROXYSULFATE

Initial millimolal concentrations					
K ₂ S ₂ O ₈ , 9.0; NH ₃ , 67.8; AgClO ₄ , 5.0; KOH, 30.0			K ₂ S ₂ O ₈ , 9.0; NH ₃ , 33.9; AgClO ₄ , 5.0; KOH, 30.0		
Time	S ₂ O ₈ ⁻ concn.	Rate const.	Time	S ₂ O ₈ ⁻ concn.	Rate const.
0	9.0	..	0	9.0	..
11	6.7	5.36	11	7.2	4.05
18	5.6	5.26	18	6.1	4.31
30	4.1	5.24	30	4.8	4.19
49	2.5	5.22	49	3.1	4.34
73	1.3	5.29	73	1.9	4.26
98	0.7	5.20	98	1.1	4.28
Mean 5.26			Mean 4.24		

In Table III are given the mean values of the rate constants for a number of experiments in which the initial concentrations of the separate substances were systematically varied.

TABLE III
MEAN VALUES OF THE RATE CONSTANTS FOR EXPERIMENTS WITH VARIED INITIAL CONCENTRATIONS OF THE REACTING SUBSTANCES

K ₂ S ₂ O ₈	Initial millimolal concentrations—		KOH	Rate constant
	AgClO ₄	NH ₃		
9.0	5.0	32.6	30.0	4.18
9.0	5.0	33.9	30.0	4.24
9.0	5.0	58.6	30.0	4.86
9.0	5.0	65.2	30.0	5.01
9.0	5.0	67.8	30.0	5.26
9.0	5.0	117.4	30.0	6.34
9.0	5.0	130.4	30.0	6.45
9.0	5.0	234.8	30.0	8.89
8.6	5.0	38.3	90.4	3.41
8.1	5.0	76.6	90.4	4.30
8.1	5.0	153.1	90.4	5.84
9.0	5.0	58.6	30.0	4.86
9.0	10.0	58.6	30.0	4.47
8.6	5.0	38.3	17.0	5.0
8.6	5.0	38.3	34.0	4.45
8.6	5.0	38.3	51.9	4.01
8.6	5.0	38.3	90.4	3.41

The Primary Reaction Determining the Reaction Rate

In Table I are given the results of two experiments which differed only in the initial concentration of ammonia. It is evident from the results that the rate of the catalyzed reaction is not independent of the concentration of ammonia, but increases with it. Since its concentration during any one experiment will decrease not only by oxidation, but also by neutralization, owing to the acid formed by the reaction, this may well account for the steady decrease in the rate constants.

The effect of neutralization was obviated in the other experiments by adding to the solutions a moderate or large excess of potassium hydroxide. When this is done, the advantages of using potassium peroxy sulfate instead of the ammonium salt are obvious. Therefore, of the experiments recorded in the tables only those in Table I were made with ammonium peroxy sulfate.

By plotting the results of the experiments given in Table II and by taking tangents at corresponding points on the curves it was found that the rate of the second experiment was only about 20% greater than that of the first, although the initial concentration of ammonia was doubled. It is evident from this that the rate of the catalyzed reaction increased much less rapidly than proportional to the concentration of ammonia.

Since the effect of ammonia is not great, it was found possible to determine the effect of peroxysulfate ion and silver diammonia ion on the rate by the methods described in the former paper. The rate of the catalyzed reaction was thus found to be directly proportional to the concentration of peroxysulfate ion and to that of silver ammonia ion.

Potassium hydroxide was also found to have a definite effect on the rate. The rate was found to decrease as the hydroxide ion concentration increased, but not inversely proportional to it. Thus it was found that a two-fold increase in hydroxide ion decreased the rate about 15%. Since both hydroxide ion and ammonia are used up during the reaction, and since their effects are in opposite directions and approximately equal in magnitude, the following differential equation may be expected to express the rate in any one reaction mixture.

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k(\text{S}_2\text{O}_8^{2-})(\text{Ag}(\text{NH}_3)_2^+) \quad (4)$$

The values of the rate-constants given in Table III were calculated from the integrated form of this equation, regarding the total peroxysulfate present as equivalent to $(\text{S}_2\text{O}_8^{2-})$, and the total silver present as equivalent to $(\text{Ag}(\text{NH}_3)_2)^{++}$. The constants show no marked trend, nor do they vary greatly from the average value.

The Effect of Ammonia on the Reaction Rate

The first two groups of experiments given in Table III were all made with the same initial concentration (0.030 or 0.090 *M*) of potassium hydroxide, but with different initial concentrations of ammonia. From the results it will be seen that an eight-fold increase in ammonia results in only a two-fold change in the value of the rate constant. By plotting the values of all the rate constants against the initial ammonia concentration minus twice the silver concentration, the two curves shown in Fig. 1 were obtained. The resulting graphs are seen to be straight lines.

Let us now take into consideration the effect that might result from the presence of the ion $\text{Ag}(\text{NH}_3)_3^+$. Considering that its rate of reaction with peroxysulfate ion may be different from that of silver diammonia ion, we may write the rate equation in the form

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k_1(\text{S}_2\text{O}_8^{2-})(\text{Ag}(\text{NH}_3)_2^+) + k_2(\text{S}_2\text{O}_8^{2-})(\text{Ag}(\text{NH}_3)_3^+) \quad (5)$$

Since the reaction $\text{Ag}(\text{NH}_3)_2^+ + \text{NH}_3 = \text{Ag}(\text{NH}_3)_3^+$ is doubtless practically an instantaneous one, we may assume that its equilibrium is established corresponding to the mass-action expression,

$$(\text{Ag}(\text{NH}_3)_3^+)/(\text{Ag}(\text{NH}_3)_2^+)(\text{NH}_3) = K \quad (6)$$

Combining (6) with (5) and simplifying, we have as the rate equation for reaction mixtures in which the initial concentration of hydroxide ion is the same,

$$-d(\text{S}_2\text{O}_8^{2-})/dt = (\text{S}_2\text{O}_8^{2-})(\text{Ag}(\text{NH}_3)_2^+)\{k_1 + k_2K(\text{NH}_3)\} \quad (7)$$

Since the concentration of ammonia in the experiments was high compared

with that of peroxy sulfate, the effect of the term $k_2K(\text{NH}_3)$ must be practically constant for any one experiment, and the straight lines of Fig. 1 are in fact the graphs that would be obtained from the equation $k = k_1 + k_2K(\text{NH}_3)$, where k is the total rate constant which appears in Equation 4.

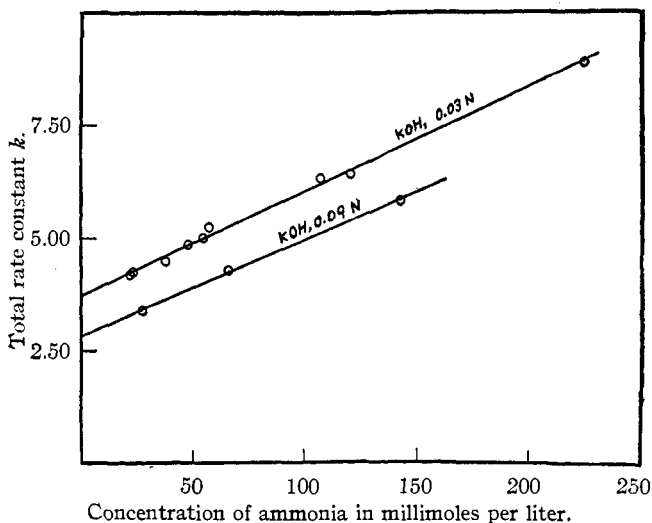


Fig. 1.

From a series of experiments, like those of Table III, there may be obtained a series of values of k and (NH_3) . The values of k_1 and k_2K might then be found by solving the corresponding simultaneous equations; but it was considered simpler and more accurate to find the value of k_1 by extrapolating the graph to zero ammonia concentration and then to calculate the value of k_2K from that of k for each experiment. The values of k_2K so found are given in Table IV for the first group of experiments (with the potassium hydroxide 0.03 M) recorded in Table III. The agreement of the k_2K values is satisfactory.

TABLE IV
VALUES OF THE PARTIAL REACTION-RATE CONSTANTS

Initial NH_3	$(\text{NH}_3 - 2\text{Ag})$	k	k_2K
32.6	22.6	4.18	21.7
33.9	23.9	4.24	22.6
58.6	38.6	4.47	20.0
65.2	55.2	5.01	23.7
67.8	57.8	5.26	26.0
117.4	107.4	6.34	24.6
130.4	120.4	6.45	22.8
234.8	224.8	8.89	23.0
48.6	48.6	4.86	23.9

These results indicate that the first slow step in the catalyzed ammonia oxidation may consist in the two simultaneous reactions: $S_2O_8^{2-} + Ag(NH_3)_2^+ = 2SO_4^{2-} + Ag^{+++} + 2NH_3$; $S_2O_8^{2-} + Ag(NH_3)_3^+ = 2SO_4^{2-} + Ag^{+++} + 3NH_3$; and that these are followed by the rapid reaction $3Ag^{+++} + 9NH_3 = 3Ag(NH_3)_2^+ + N_2 + 6H^+$. Since K is small and k_2K large, it follows that the rate constant k_2 of the second reaction is much larger than the rate constant k_1 of the first reaction.

Others have previously considered that the total rate of oxidation may be the sum of two or more partial rates that refer to different compounds containing the oxidized or reduced element in different forms. Thus Mitchell⁶ found that the results of his experiments on the rate of the reaction between phosphorous acid and iodine can be explained by assuming two isomeric forms of orthophosphorous acid, one of which reacts with I_2 and the other with I_3^- , each reaction having a different rate; and it has been found by Spitalsky⁷ that chromate ion and dichromate ion have different effects on the rate of decomposition of hydrogen peroxide, though the effect in mixtures is not very clear-cut. The simple example offered by the present research seems representative of this phenomenon.

At this point may be mentioned the reasons for rejecting certain other mechanisms that might at first sight seem possible. Such mechanisms might involve (1) a slow reaction between trivalent silver and ammonia, or (2) formation of a moderately stable complex of the type $Ag(NH_3)_m^{+++}$, which slowly decomposes with evolution of nitrogen and production of silver ion and hydrogen ion. These two possibilities are disposed of in turn by the following experimental facts. (1) Though trivalent silver oxide (Ag_2O_3) is only very slightly soluble in neutral or alkaline solutions, yet no precipitate of it appears during the reaction. (2) When the freshly prepared oxide is mixed with solutions of ammonia, it decomposes with evolution of nitrogen, but seems to dissolve only to the extent to which it has decomposed. Evidently, if the reaction between Ag^{+++} and ammonia were slow, Ag^{+++} would accumulate and a precipitate of silver sesquioxide would form, since a complex $Ag(NH_3)_m^{+++}$ does not form, as shown by the second of these facts.

The Effect of Hydroxide Ion on the Reaction Rate

The initial concentrations of ammonia were the same in the third group of experiments recorded in Table III, but that of potassium hydroxide was varied. The effect of the potassium hydroxide, while not great, is still much too great to be ascribed to the decreases in activity coefficients caused by it. When the rate constants are plotted against the initial concentration of potassium hydroxide, the resulting graph is not a straight

⁶ Mitchell, *J. Chem. Soc.*, **123**, 2241 (1923).

Spitalsky, *Z. anorg. Chem.*, **53**, 184 (1907).

line, as may be seen from the curve in Fig. 2. The effect may be due to the fact that hydroxide ion unites with $\text{Ag}(\text{NH}_3)_2^+$ to form the un-ionized base $\text{Ag}(\text{NH}_3)_2\text{OH}$, and that its rate of reaction with peroxysulfate ion is lower than that of $\text{Ag}(\text{NH}_3)_2^+$ or $\text{Ag}(\text{NH}_3)_3^+$. This simple explanation cannot be regarded as complete, however, since rate Equation 5, when modified by the addition of a negative term $-k_3K(\text{OH}^-)(\text{Ag}(\text{NH}_3)_3^+)(\text{S}_2\text{O}_8^{2-})$, does not fit the experimental facts. It is possible, nevertheless, that this is because a decrease in the activity coefficient of peroxysulfate ion is superposed upon the effect of producing a less reactive substance. There is, however, no independent experimental evidence as to the degree of ionization of the silver ammonia hydroxide.

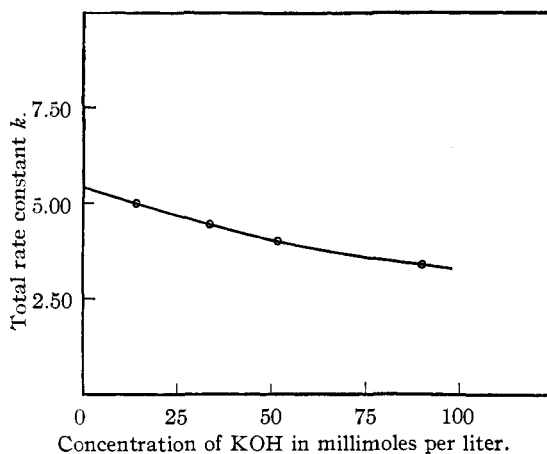


Fig. 2.

Comparison of the Rates of the Oxidation of Chromium and of Ammonia

It has been shown that the slow step in the silver salt catalysis of the chromium and ammonia oxidations consists in the oxidation of the univalent silver ion to trivalent silver. Since there seems to be no essential difference between a hydrated ion and an ammoniated one, it is natural to inquire whether the group present in the silver complex has an appreciable effect on the rate of oxidation of the silver which is the essential constituent of the ion from the oxidation viewpoint. The results described in this paper and the former one lead to the conclusion that the effect is a marked one. In the case of the simple hydrated silver ion, such as is present in the acid solution used for the chromium reaction, the rate constant was found to be 0.333, while in the case of the silver ammonia complex, the constant is more than ten times as large. Moreover, the increase in rate with the number of ammonias present in the complex, and its decrease on the addition of an hydroxide ion are further evidences that

the rate of reaction of complex ions containing a common oxidizable element depends considerably on the nature of the groups present.

Summary

The rate of the reaction between peroxysulfate ion and ammonia, when catalyzed by silver salts, has been measured and found to be directly proportional to the concentrations of peroxysulfate ion and silver ammonia ion. The rate was also found to increase with the concentration of ammonia, and decrease with that of hydroxide ion, but not to be directly proportional to the former, nor inversely proportional to the latter. To explain the effect of ammonia it was concluded that, inasmuch as silver triammonia chloride $\text{Ag}(\text{NH}_3)_3\text{Cl}$ exists as a solid phase, the ion $\text{Ag}(\text{NH}_3)_3^+$ probably exists in solution (though in small amounts) and that peroxysulfate ion S_2O_8 reacts with it at a rate different from that with $\text{Ag}(\text{NH}_3)_2^+$. The experimental results were found to be in accord with this conclusion. It was also shown that the effect of ammonia could not be explained as due to a slow reaction between the trivalent silver ion and ammonia, since freshly prepared silver sesquioxide reacts rapidly with ammonia. It is suggested that the effect of hydroxide ion may be due in part to the formation of the un-ionized compound $\text{Ag}(\text{NH}_3)_2\text{OH}$, and that this reacts more slowly with peroxysulfate ion than does $\text{Ag}(\text{NH}_3)_2^+$, and in part to the decrease in the activation of peroxysulfate ion caused by it. According to these explanations the slow steps of the catalyzed reaction consist of three simultaneous reactions involving the oxidation by peroxysulfate ion of $\text{Ag}(\text{NH}_3)_2^+$, of $\text{Ag}(\text{NH}_3)_3^+$, and of $\text{Ag}(\text{NH}_3)_2\text{OH}$, to trivalent silver ion, Ag^{+++} ; and the rapid and final step is the reaction between trivalent silver and ammonia to produce nitrogen, silver ion and acid.

A comparison of the rates of the catalyzed chromium and ammonia reactions showed that silver when present in the form of silver ammonia reacts more than ten times as fast with peroxysulfate ion as it does when present as hydrated silver ion. This fact shows that the rates of reactions involving various compounds of a reacting element may depend to a large extent on the nature of the groups attached to the element.

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