[Contribution from the Department of Chemistry, Washington Square College, New York University]

# SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. V. A QUANTITATIVE STUDY OF THE OXIDATION OF AMMONIA[1]

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## Introduction

It was first shown by Marshall[2] that ammonia is oxidized to free nitrogen by persulfate, in the presence of silver salts. Marshall assumed that this reaction was quantitative, or nearly so, without making any extended investigation of the matter; while he found a trace of oxygen in the gas evolved, he attributed this to the accidental admixture of some air. Marshall also showed that ammonium ion, in neutral or acid solution, is oxidized to nitrate ion,[3] and this he proved to be practically quantitative except in strongly acid solution.

Yost, in a study of the velocity of the oxidation of ammonia by persulfate and silver ions,[4] assumed that the oxidation to free nitrogen was quantitative in solutions containing ammonia with or without added alkali (KOH), and the same assumption was made by King[5] in the first paper of this series, without further inquiry.

The original purpose of the present investigation was to determine the concentrations of ammonia and ammonium ion, or the hydrogen-ion concentration, of the solutions in which the oxidation to nitrate begins to replace the oxidation to free nitrogen. However, as will be seen below, it unexpectedly developed that the production of nitrogen is quantitative in a very limited concentration range, and, it therefore, became the purpose of this work to investigate the effect of various substances on the amount of nitrogen evolved.

It is assumed that when ammonia or ammonium ion is oxidized, only the two substances mentioned are produced, according to the following equations

$$2NH_3 + 3S_2O_8^{=} \longrightarrow N_2 + 6SO_4^{=} + 6H^+ \quad (1)$$

$$NH_4^+ + 4S_2O_8^{=} + 3H_2O \longrightarrow NO_3^- + 8SO_4^{=} + 10\,H^+ \quad (2)$$

It is unlikely that other possible products could exist in appreciable amounts in the presence of persulfate and silver ions. While oxygen is produced by the action of persulfate on water, the reaction is so slow as to be negligible under the conditions of these experiments.

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[1] This paper summarizes a thesis presented by F. L. Griswold to the Graduate Faculties of New York University in partial fulfilment of the requirements for the degree of Master of Science.

[2] Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900).

[3] Marshall, *ibid.*, **24**, 88 (1902).

[4] Yost, This Journal, **48**, 374 (1926).

[5] King, *ibid.*, **49**, 2689 (1927).

It will be seen that after the persulfate has all disappeared, the extent of both reactions can be estimated by any one of three methods: (1) estimating the nitrate produced, (2) titrating the unoxidized and un-neutralized ammonia remaining, or the acid produced, or (3) measuring the volume of nitrogen produced. Of these, the third was selected as being sufficiently accurate and by far the easiest.

## Materials and Experimental Procedure

Potassium persulfate was recrystallized until free from sulfate. C. P. ammonia water was diluted to the desired strength and standardized against hydrochloric acid. Ammonium nitrate was recrystallized and dried in a desiccator. Standard solutions of silver nitrate, potassium nitrate and sodium hydroxide were prepared from C. P. materials.

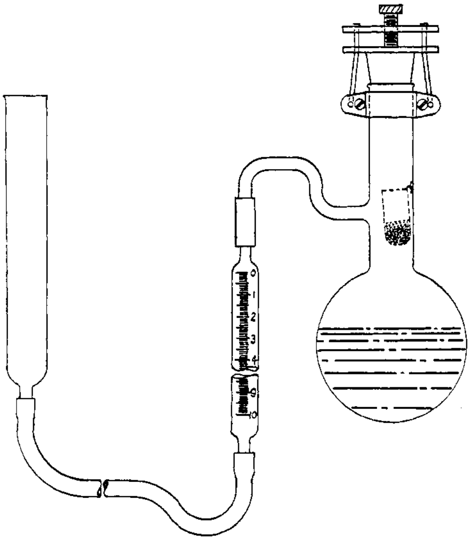

Fig. 1.

Standard solutions of the reagents desired, except the persulfate, were pipetted into the reaction flask shown in Fig. 1 and made up to 100 cc. The exact amount of potassium persulfate (0.1809 g.) to liberate 5 cc. of nitrogen at standard conditions was carefully weighed into a glass capsule and hung on a platinum loop in the neck of the reaction flask. The flask was sealed, the persulfate shaken down and dissolved, and the apparatus allowed to stand until no more nitrogen was evolved (usually twenty-four hours were allowed, sometimes forty-eight). The nitrogen volume was noted by readings on the attached gas buret before and after the reaction, and then corrected to 0° and 760 mm. Corrections were made, of course, for change in the total volume of air and nitrogen in the entire gas space (approx. 65 cc.) when there was any change in atmospheric pressure during the experiment, and for the vapor pressure of water and ammonia above the solutions. The flask was thoroughly shaken before the final reading to avoid supersaturation.

All experiments were carried out at 25 ± 0.02° by immersing the entire apparatus in a large thermostat. The particular persulfate concentration to evolve theoretically 5 cc. of nitrogen was chosen because it is close to some of the values used by Yost and by King, and also because with the apparatus chosen this amount was convenient and gave a suitable degree of accuracy (± less than 1% in most of the experiments). While only experiments with this persulfate concentration are reported here, preliminary experiments with other concentrations gave similar results.

## Results of Experiments and Discussion

The results of all the experiments are given in Table I and are shown graphically in Fig. 2, where average values of the duplicates given in the table are plotted. The volumes given are cc. of nitrogen (corrected to standard conditions) evolved at 25°, the theoretical value being 5 cc., *i. e.*, if all the persulfate disappeared according to Equation 1. Three concentrations of silver nitrate, 0.04 *M*, 0.02 *M* and 0.005 *M* were used; 0.04 *M* silver nitrate will, of course, require 0.08 *M* ammonia to form the silver diammonia ion. About 0.0045 *M* ammonia in addition is required for the oxidation by Equation 1 and 0.013 *M* ammonia to neutralize the hydrogen ion produced, making about 0.1 *M* ammonia necessary to leave any excess. Some nitrogen is produced with even less than 0.08 *M* ammonia, but the theoretical amount is not produced even with 0.1 *M* or more concentrated ammonia (see Col. 2 in the table).

Table I

Cc. of Nitrogen (Corrected to 0° and 760 Mm.) Evolved at 25° from 100 Cc. Solution of Concentrations Shown. $K_2S_2O_8$ 0.00667 *M* in all Experiments

| $C_{NH_3}$ | $AgNO_3$, 0.04 *M* | | | $AgNO_3$, 0.02 *M* | | $AgNO_3$, 0.005 *M* | | $AgNO_3$, 0.0033 *M* NaOH |
|---|---|---|---|---|---|---|---|---|
| | | $NH_4NO_3$, 0.025 *M* | $KNO_3$, 0.04 *M* | | $NH_4NO_3$, 0.1 *M* | | $NH_4NO_3$, 0.1 *M* | |
| | 1.96 | | 1.73 | 2.08 | 3.26 | 3.67 | 3.75 | (0.1 *M*) |
| | 1.93 | | 1.78 | | 3.28 | 2.52 | 4.19 | |
| 0.0265 | 1.99 | | | | | 3.79 | 4.43 | 1.85 |
| | 1.91 | | | | | 3.77 | 4.48 | 1.63 |
| | 2.86 | 3.13 | | 3.96 | 4.56 | 4.12 | 4.92 | (0.04 *M*) |
| | 2.72 | 2.72 | | 3.78 | | 4.21 | 4.87 | |
| .053 | 2.30 | 2.55 | | | | 3.91 | | 2.16 |
| | 2.30 | 2.53 | | | | 3.98 | | 2.11 |
| | 3.93 | 4.11 | | 4.37 | 4.99 | 4.41 | 4.90 | (0.1 *M*) |
| .106 | 4.25 | 4.47 | | 4.37 | 4.94 | 4.36 | 4.94 | 2.75 |
| | | | | | | | | 2.88 |
| | 4.70 | 4.85 | | 4.43 | 4.88 | 4.51 | 5.05 | |
| .265 | 4.75 | | | 4.43 | 4.91 | 4.62 | 5.05 | |
| | 4.80 | | | | | | | |
| | 4.57 | | | | | | | |
| | 4.81 | 4.79 | | 4.60 | 4.87 | 4.54 | 5.02 | |
| .53 | 4.73 | 4.82 | | 4.59 | 4.93 | 4.52 | 5.02 | |
| | | 4.80 | | | | | | |
| 4.5 | | | | | | 4.13 | 4.01 | |
| | | | | | | 3.96 | 4.10 | |

Thus it appears that ammonia can be oxidized even though the amount in the solution is stoichiometrically unable to satisfy the silver ion, but it is evident that nitrogen alone is not produced *below* some definite hydrogen-ion concentration and nitrate ion alone *above* this hydrogen-ion concentration. Since the persulfate all disappeared in these experiments, the two reactions must proceed simultaneously, probably from the start. The experiments with lower silver-ion concentrations gave similar results. With 0.02 *M* silver nitrate, about 0.06 *M* ammonia is necessary to leave any excess. However, the theoretical amount of nitrogen is not liberated with any ammonia concentration up to 0.53 *M* (Col. 5 in the table). The same is true for 0.005 $M$ silver nitrate (Col. 7 in the table). With low concentrations of ammonia, less silver nitrate gives more nitrogen; with higher ammonia concentrations, the reverse is true.

It was expected that addition of sodium hydroxide would increase the evolution of nitrogen. The last column of the table shows that the reverse is true. No comparative experiments were run with 0.0033 $M$ silver nitrate and no sodium hydroxide, but it can easily be predicted from the table and curves that more nitrogen would be evolved.

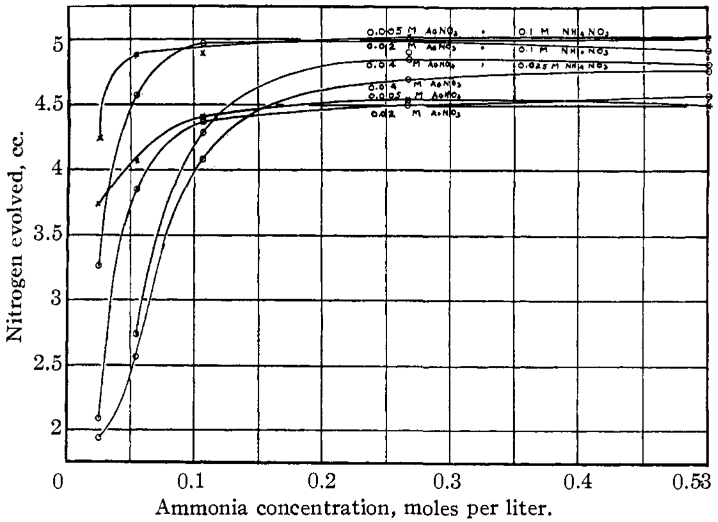

Fig. 2.—Volume of nitrogen evolved at 25° (corrected to 0° and 760 mm.) from 100 cc. of solution containing 0.00667 $M$ $K_2S_2O_8$ and other reagents as shown. The concentration scale is compressed slightly at the extreme right.

According to Marshall[2,3] and experiments described in the first paper of this series, no nitrogen is liberated from a neutral or acid solution of an ammonium salt, and this was verified by experiments carried out by the method used here. The addition of an ammonium salt increases the hydrogen-ion concentration as well as the ammonium-ion concentration. It was, therefore, expected that addition of ammonium nitrate would decrease the amount of nitrogen produced, and increase the proportion of nitrate formed; just the opposite effect was observed, as is shown by the values in Cols. 3, 6 and 8 of the table and by the curves in Fig. 2. This is true for most of the curve with 0.04 $M$ silver nitrate, with only 0.025 $M$ ammonium nitrate, and the effect is especially pronounced with the 0.02 $M$ and 0.005 $M$ silver nitrate and 0.1 $M$ ammonium nitrate. It will be noticed that *only these solutions with the lower silver nitrate concentrations and considerable added ammonium nitrate approach the theoretical evolution of* *nitrogen.* In the solutions with 0.02 *M* silver nitrate the 5 cc. is scarcely reached (within experimental error) but with 0.005 *M* silver nitrate and 0.1 *M* ammonium nitrate it is certain that for some of the ammonia concentrations the reaction is quantitative according to Equation 1.

It was thought possible that this increase in nitrogen evolution by ammonium nitrate was a general effect that would be produced by the addition of any inert salt. For this reason two experiments were run with the addition of potassium nitrate, but as is seen in Col. 4 of the table, potassium nitrate actually decreases the evolution; the effect of ammonium salts is a specific one.

Some of the values for 0.53 *M* ammonia are slightly lower than the values for lower ammonia concentrations. The difference is almost within experimental error, but a few experiments with 4.5 *M* ammonia confirmed the suspicion that the amount of nitrogen produced reaches a maximum and thereafter falls off with increasing ammonia concentration. These results are shown in the table but not on the curves in Fig. 2.

## Conclusions

It is impossible to say definitely whether some ammonium ion is oxidized to nitrogen in the slightly alkaline solution (although it is not in neutral or acid solution) and that this accounts for the effect of added ammonium ion, or whether the increase in hydrogen-ion concentration brings about increased oxidation of ammonia itself to nitrogen.

The most obvious conclusion is that Yost and King, in their experiments (referred to above), did not meet the conditions necessary for the theoretical evolution of nitrogen. While the experiments here do not duplicate their concentrations exactly, it is easily seen that even in their experiments with no alkali added the nitrogen evolution could scarcely be over 80% of the theoretical, and with added hydroxide it must have fallen as low as 50%. Yost measured the rate of disappearance of persulfate and consequently the sum of Reactions 1 and 2; King measured the rate of evolution of nitrogen, and assumed in calculating velocity constants that this was proportional to the rate of disappearance of persulfate. Thus their measurements are undoubtedly valid when it is remembered that the slow reaction is probably that between persulfate and silver ions, whether nitrogen or nitrate is produced later, but the fact that neither product is formed quantitatively must always be considered before the results are used for other than comparative purposes.

## Summary

Measurements of the volume of nitrogen evolved when ammonia is oxidized by persulfate ion in the presence of silver ion show that: (1) the theoretical amount of nitrogen is produced only under a very limited range of concentrations of ammonia, ammonium ion and silver ion; (2) the

addition of ammonium nitrate increases the volume of nitrogen evolved; (3) the addition of sodium hydroxide or potassium nitrate decreases the amount of nitrogen evolved; (4) although nitrogen is produced when less than enough ammonia is present to form the silver diammonia ion, a large excess of ammonia is necessary to give the maximum nitrogen evolution. With still higher ammonia concentrations the amount of nitrogen produced decreases again. (5) Yost, and King were unjustified in assuming that in their experiments the disappearance of persulfate was due to one reaction only.

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# THE ELECTRON AFFINITY OF FREE RADICALS. I. THE ELECTRON AFFINITY OF TRIPHENYLMETHYL

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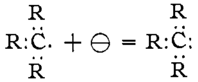
The elementary process of removing an electron from an atom involves an energy change which is related to both the nuclear charge and the electronic configuration of the atom. Millikan and Bowen[1] have shown the energy to be a linear function of the square of the nuclear charge in systems containing the same number of electrons. A study of the electron affinities of free radicals offers the opportunity of keeping the nuclear charge and the number of electrons constant while studying the effect of varying the groups which share six of the electrons of the atom. Thus in the reaction



$$\mathrm{R}:\overset{\mathrm{R}}{\underset{\ddot{\mathrm{R}}}{\ddot{\mathrm{C}}}}\cdot + \ominus = \mathrm{R}:\overset{\mathrm{R}}{\underset{\ddot{\mathrm{R}}}{\ddot{\mathrm{C}}}}:$$

the measurement of $\Delta H$ for various radicals should enable one to determine to what extent the addition of an electron to an odd molecule to form an electron pair is affected by a change in the configuration of the rest of the electrons in the molecule. This paper describes the procedure and gives the data for triphenylmethyl.

The reaction chosen for study is that of the addition of sodium to triphenylmethyl

$$\mathrm{Na} + \mathrm{R} = \mathrm{Na}^+ + \mathrm{R}^-$$

in which R represents triphenylmethyl. The free energy change accompanying this reaction may be obtained directly from the equilibrium constant for the reaction provided experimental conditions can be found for establishing an equilibrium and determining the activities of the various molecular and ionic species. The large deviation from perfect solution shown by sodium amalgams suggested the possibility of using them in

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[1] Millikan and Bowen, *Proc. Nat. Acad. Sci.*, **13**, 531 (1927).