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Mechanisms of Oxidation of Nitrogen Nucleophiles by Peroxodisulfate Ion: Nitrite Ion and Ammonia

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Abstract

The particular set of reactivities of nitrogen donors and of peroxodisulfate that make their interactions mechanistically complicated are discussed. Two reactions of this class have been studied experimentally. In the oxidation of nitrite ion by peroxodisulfate, the nitrogeneous product is nitrate. The rate law:

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-]$$

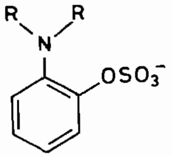
has been found. A significant change in rate on addition of allyl alcohol to the system indicates the presence of free radicals to an extent greater than can be ascribed to the k_1 term alone. The possible intervention of NO_2 as an intermediate has been investigated. Mechanisms for the two oxidation paths are proposed. The reaction of peroxodisulfate with ammonia and ammonium ion gives dinitrogen. Radical (but not chain) paths were found as indicated by rate law (first order in peroxodisulfate and zero order in reductant), rate constants, and activation parameters. Copper(II) catalysis by a free radical chain process occurs in the ammonia oxidation.

Introduction

Peroxide reactions occur by polar and free radical mechanisms, and oxidation of nitrogen donors with peroxodisulfate ion (hereafter persulfate) presents one with the possibility of comparing the rates of the two mechanistic types in a single solution. Persulfate reacts near room temperature with polarizable nucleophiles such as iodide ion and dialkyl sulfides by second-order displacement processes having low value of $\Delta H^{\ddagger}$ (usual range 50 to 100 kJ mol^{-1}) and negative $\Delta S^{\ddagger}$ (usual range −40 to −120 J mol^{-1} K^{-1}). However radicals formed by homolytic scission of persulfate dominate the mechanisms at temperatures of 60 °C or higher. Radical oxidations are important for oxygen compounds (H_2O, H_2O_2) and many organics (alcohols, ethers, carboxylic acids); these reductants have only weakly polarizable sites although they may be basic to protons. Some of the radical mechanisms involve long chains (*e.g.*, isopropyl alcohol) whereas others do not, with water oxidation being the paradigm of a non-chain mechanism. The characteristics of chain and non-chain radical reactions are mentioned below. The oxidation mechanisms of persulfate have been reviewed [1–4].

Nitrogen reductants are intermediate in polarizability between sulfur and oxygen compounds, so it is difficult to predict the mechanisms by which donors would be oxidized by persulfate. Suffice it to say that nitrogen nucleophiles have reactivities lower than iodide ion, of comparable size to bromide ion, and larger than chloride ion. Comparison of nitrite ion data with those of bromide ion will be made in the Discussion, as will that of ammonia with water and chloride ion.

The difficulty in predicting oxidation mechanisms for nitrogen compounds can be seen by a study of the literature on mechanisms of aniline oxidations by persulfate [5]. In most instances an ortho-sulfato product is formed, however the point of first attack



by persulfate on the reductant could be any of one of the following three atoms: the nitrogen, the *ipso* carbon, or the *ortho* carbon, followed by migration to the *ortho* carbon in the first two cases. Electronic effects of ring substituents indicates that sulfate group migration after the rate step is operative.

Studies on persulfate oxidation of nitrite ion and ammonia are presented here. Other compounds

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were checked during the investigation. It will be necessary to compare the results obtained with the numerical data and mechanism for water oxidation, thus a brief review is necessary here; a detailed review is available elsewhere [4].

Kolthoff and Miller [6] after study of water oxidation postulated the mechanism here given in a simplified form. The last step appears to compete with:

$$S_2O_8^{2-} \xrightarrow{k_{1a}} 2SO_4^{\cdot-}$$

$$SO_4^{\cdot-} + H_2O \xrightarrow{k_{2a}} HSO_4^- + HO\cdot$$

$$2HO\cdot \xrightarrow{k_{3a}} H_2O_2$$

$$S_2O_8^{2-} + H_2O_2 \xrightarrow{k_{4a}} O_2 + 2HSO_4^-$$

the alternative:

$$2H_2O_2 \xrightarrow{k'_{4a}} O_2 + 2H_2O$$

Depending on which last step obtains, the overall constant for water oxidation $k_{a(obs)}$ can have the value $2k_{1a}$ or k_{1a} respectively. Some important aspects of the water oxidation are: 1) the reaction is first order in persulfate concentration, 2) the mechanism is of radical nature but does not involve chains, and 3) $\Delta H^{\ddagger}$ is 134 ± 2 kJ mol^{-1} and $\Delta S^{\ddagger}$ is positive. Some detailed questions of the water oxidation are unresolved, but there now appears to be agreement on the general sequence of steps [4].

For any oxidation by persulfate similar to the water oxidation in that there is no chain even though homolytic scission of persulfate transpires, $\Delta H^{\ddagger}$ should be near to that of water. Both rate constant and $\Delta S^{\ddagger}$ can differ somewhat as a result of stoichiometry. When a radical chain comes into play, the value of $\Delta H^{\ddagger}$ will range between 70 and 140 kJ mol^{-1}. Also the chain oxidations have some or all of the following characteristics: 1) rates significantly greater than that for water oxidation, 2) inhibitions, 3) induction periods, and 4) trace metal catalysis.

Important to the nitrite ion oxidation rates are the corresponding bromide ion data. Some relevant numbers from the literature are presented in Table I. Most of the rates have been collected previously [7, 8]. It is to be noted that nitrite ion is less reactive than bromide for four peroxides, as it is for oxidation by hypochlorous acid [9] and for the postulated intermediate peroxo-periodic acid [7, 10]. The results of the present investigation give the first case where nitrite reacts more rapidly than bromide. The comparison of nitrite and bromide rates is of particular interest because these two ions have similar nucleophilic reactivities, 1.73 and 1.51 on the En scale respectively [11]; this indicates that they should react with peroxides by nucleophilic attack with similar rate constants.

TABLE I. Relative Rates for Peroxide Oxidation of Two Anions[a].

Peroxide	k_2 for NO_2^-	k_2 for Br^-
HSO_5^-	0.31 (25 °C)	1.04 (25 °C)
CH_3CO_3H	3.4×10^{-2} (25 °C)	0.258 (25 °C)
$H_2PO_5^-$	7×10^{-4} (25 °C)	2×10^{-3} (25 °C)
H_2O_2	3×10^{-7} (25 °C)	4×10^{-7} (25 °C)
$S_2O_8^{2-}$	7×10^{-4} (75 °C)	2×10^{-4} (75 °C)

[a] Rate constants have units of M^{-1} s^{-1}.

Nitrite Ion Oxidation

Background

To our knowledge, the reaction of nitrite with persulfate has not been studied previously. Work with other peroxides [7, 10, 12] and hypohalous acids [9, 13] indicated that nitrite ion does act as a nucleophile in displacement on electrophilic oxygen and that an oxygen atom is transferred to the nitrite to form nitrate.

Bromide ion reacts with persulfate [1, 14] with a two-term rate law

$$\frac{-d[S_2O_8^{2-}]}{dt} = \{k_1 + k_2[Br^-]\}[S_2O_8^{2-}]$$

and mechanisms consistent with known chemistry were proposed [1].

Stoichiometry

Using the three wavelengths 260, 300 and 353 nm, it is possible to determine NO_2^-, $S_2O_8^{2-}$ and product NO_3^- at the same time during a reaction [15]. Some results are shown in Fig. 1. In a number of experiments, it was found that the reaction conformed closely to the stoichiometry

$$S_2O_8^{2-} + NO_2^- + H_2O \longrightarrow 2SO_4^{2-} + NO_3^- + 2H^+$$

The averaging of a series of spectrophotometric experiments gave the value of 0.96 ± 0.02 for $[NO_2^-]$ lost/$[S_2O_8^{2-}]$ lost; a similar calculation for $[NO_3^-]$ formed/$[NO_2^-]$ lost gave 0.98 ± 0.02. The ±0.02 does not include all possible errors, so it is concluded that each value probably is unity within our experimental error.

It is to be noted that the reaction generates acid. This was confirmed by the appearance of the spectrum of nitrous acid when nitrite and persulfate

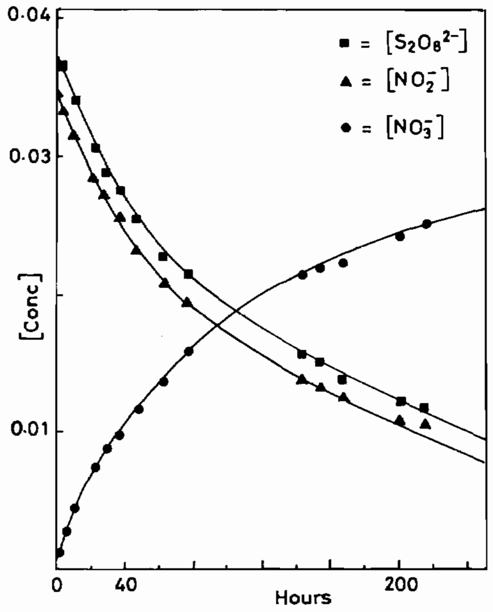


Fig. 1. Concentration changes of $S_2O_8^{2-}$, NO_2^- and NO_3^- during one kinetic run.

were mixed. Therefore all kinetic runs were carried out in $H_2PO_4^-$ and HPO_4^{2-} buffer well above the pH of protonation of nitrite. Phosphate was chosen because it has no known reaction with any of the species present.

Kinetics

The reaction was normally followed by the disappearance of persulfate because it was found that the reaction is first order in persulfate as indicated by linear log persulfate concentration against time plots up to three half-lives. Also variation in initial persulfate concentration did not alter the pseudo-first-order constant k_{obs}.

The rate of the reaction is not greatly larger than the rate of persulfate oxidation of water, therefore the homolysis of the peroxide is likely to contribute to the total rate. The order in nitrite, as indicated from initial concentration variation, ranged from 0.6 to 0.8, suggesting a two-term rate law. Such is the case as seen in Fig. 2 where, for k_{obs} plotted against nitrite concentration, the data give a linear slope plus an intercept.

The rate was not dependent on pH over the range 6.7 to 9.9 [8], which is almost a factor of 2000 in hydrogen ion concentration.

The complete rate law is:

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-]$$

which is the same type as seen for the bromide ion oxidation by persulfate. The values of k_1 obtained from initial sets of data ranged from 2 to 4 X 10^{-6} s^{-1}; the Fig. 2 data give 3.1 X 10^{-6} s^{-1}. This may be compared with the accepted value of 5.0 X 10^{-6} s^{-1} for water oxidation at 60 °C [4]. Values of k_2 were 0.48 X 10^{-4}, 1.10 X 10^{-4} and 2.25 X 10^{-4} M^{-1} s^{-1} at 40°, 50° and 60 °C, respectively. From these data $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated as 71 kJ mol^{-1} and −76 J mol^{-1} K^{-1}, respectively.

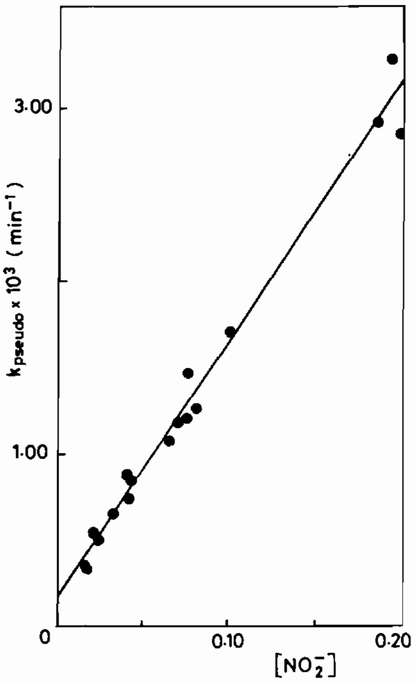


Fig. 2. Dependence of the pseudo-first-order rate constant for persulfate loss on nitrite ion concentration.

Nitrogen Dioxide Oxidation

The first-order term has a rate constant clearly indicative of persulfate homolysis. This is presumably followed by the fast step:

$$SO_4^{\cdot-} + NO_2^- \longrightarrow SO_4^{2-} + NO_2\cdot$$

in view of the known relative stability of nitrogen dioxide in spite of its radical nature. No evidence for free $NO_2\cdot$ was found in our solutions [8]. One can then test experimentally whether this radical will attack persulfate directly under our conditions. This was done by passing $NO_2\cdot$ into an aqueous buffered persulfate solution and comparing the results with experiments where $NO_2\cdot$ was passed into buffered water. It was found that no persulfate was used up and that the final ratio of nitrite to nitrate concentrations did not depend on the persulfate present [8].

We conclude that $NO_2\cdot$ reacts with water faster than with persulfate. This means any mechanism postulated can not have the step:

$$NO_2\cdot + S_2O_8^{2-} \xrightarrow{H_2O} NO_3^{-} + SO_4^{2-} + SO_4^{\cdot -} + 2H^+$$

or equivalent. By extension $NO_2\cdot$ is excluded as a chain carrier.

Radical Trapping Experiments

The presence of $SO_4^{\cdot -}$ and $NO_2\cdot$ in the reacting solution is probable even if only as part of the first-order mechanism. Allyl acetate is polymerized by aqueous persulfate under our conditions, however no polymer was formed when nitrite was also present. Unfortunately no satisfactory analytical procedure for determining nitrite concentration in the presence of allyl acetate could be found, so no further experiments with this olefin were carried out.

Allyl alcohol which gives a soluble polymer and for which no absorption above 300 nm was found allows a spectra study of nitrite disappearance rate, although there is serious competitive reaction of this monomer with persulfate. In a series of seven comparison experiments, it was found that the allyl alcohol decreased the rate of nitrite ion disappearance by about 80% [8]. This is considerably more than would be accounted for by the first-order term alone. Although a change in stoichiometry for the second-order term due to the presence of allyl alcohol was not expected, it must be considered. This has significant consequences in terms of proposed mechanisms.

Nitrite Oxidation Mechanisms

The order of the k_1 term suggests that this process is related to the homolytic scission of persulfate, and the value of the relevant rate constant confirms the suggestion. The mechanism most certainly is of the type:

$$S_2O_8^{2-} \xrightarrow{k_{1a}} 2SO_4^{\cdot -} \qquad \text{(slow)}$$

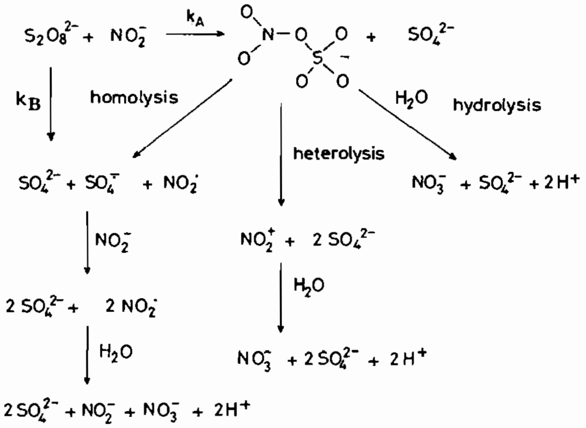
$$SO_4^{\cdot -} + NO_2^{-} \longrightarrow NO_2\cdot + SO_4^{2-} \qquad \text{(fast)}$$

$$2NO_2\cdot + H_2O \longrightarrow NO_3^{-} + NO_2^{-} + 2H^+ \qquad \text{(fast)}$$

Based on the best value of Behrman and Edwards [4] at 2.6 X 10^{-6} s^{-1} and of Kolthoff and Miller [6] at 2.8 X 10^{-6} s^{-1} for $k_{a(obs)}/2$, we feel that the value obtained for k_1 here of 3.1 X 10^{-6} s^{-1} at 60 °C is very strong proof for the mechanism postulated for this first-order term. Indeed, the quantitative agreement is so good that it points to the k_{4a} step as the final step in water oxidation in neutral solution.

By way of contrast, the other term does not lead to postulation of only one mechanism. Rather the evidence indicates that competitive paths leading to the same products must be considered. Facts which must be accommodated include the following: (1) the second-order law, (2) the activation parameters, (3) the striking decrease in the absolute value of $-d[NO_2^-]/dt$ when allyl alcohol is present, and (4) the observation shown in Table I that the second-order path for nitrite oxidation by persulfate has a much larger constant than that for bromide ion oxidation (while for the six related oxidants bromide reacts more rapidly). Again the stability of nitrogen dioxide seems relevant.

All of these facts can be interpreted provided it is assumed that for the k_2 term two competitive transition states of identical composition (except possibly for solvent) are present. The complete mechanism is given in Scheme 1. The observed second-order constant is thus the sum of k_A and k_B, but only k_A is strictly analogous to a nucleophilic displacement process and is to be compared to the bromide rate. Second-order rate initiation steps such as the k_B portions are not usually observed with persulfate, however the stability of $NO_2\cdot$ would significantly enhance the possibility of this instance. The possibility of competitive second-order paths has been seriously considered before in persulfate reactions [1, 16].



Scheme 1.

Allyl alcohol and/or its polymerizing radical (symbolized $RCH_2\cdot$) must react with one or more intermediates ($NO_2\cdot$, $SO_4^{\cdot -}$, $O_2NOSO_3^-$, NO_2^+) formed during the oxidation. For example, the radicals formed in the k_B part (and in the first-order term) could regenerate nitrite by steps such as:

$$\text{allyl alcohol} + SO_4^{\cdot -} \longrightarrow RCH_2\cdot$$

$$RCH_2\cdot + NO_2\cdot + H_2O \longrightarrow RCH_2OH + NO_2^{-} + H^+$$

If the k_B part is a power of ten more important than the k_A part (and this magnitude is consistent with the rate anomaly), then the observed reduction in nitrite disappearance rate can be rationalized.

One might well say something about mixed anhydride intermediate $O_2NOSO_3^-$. It is well established that nitric anhydride can cleave homolytically

$$N_2O_5 \longrightarrow NO_2\cdot + NO_3\cdot$$

in the gas phase and heterolytically on condensation to the solid which is known to be nitronium nitrate $NO_2^+NO_3^-$. The two cleavage reactions of $O_2NOSO_3^-$ are quite analogous, and thus NO_2^+ is indeed a possible intermediate which could be reduced by the allyl alcohol to nitrite ion [17].

Nitrogen(–III) Oxidation

Background

The nucleophilic reactivity of ammonia is relatively low (about 1.36 compared to 1.73 for nitrite [18]) and its basicity is sufficiently large that it exists as unreactive ammonium ion in neutral solution. It is not surprising then that no simple reaction with peroxide oxidants has been reported.

Because ammonium persulfate is a known industrial chemical which slowly decomposes, the oxidation of ammonia and ammonium ion has been studied a number of times. Levi and Migliorini [19] investigated the non-gaseous oxidation products, particularly nitrate ion, formed during the decomposition of ammonium persulfate with an without the addition of acid and base. On the basis of careful analytical experiments, they concluded: 1) that nitrate was formed in amounts less than stoichiometric, 2) that dinitrogen gas was a probable other product, and 3) that impurities significantly affected the reaction. The last conclusion is remarkably foresighted in view of the lack of knowledge about reaction mechanisms in 1908.

Liegeois [20] surveyed the rate of decomposition of ammonium persulfate in borax buffer. The rate was roughly first order in persulfate with a constant about a factor of two larger than that found for alkali persulfates. The activation energy (about 142 kJ mol^{-1}) was reported.

Stoichiometry

Levi and Migliorini [19] analyzed for oxoacid (the sum of presumed nitrite and nitrate). With only ammonium persulfate, they reported that about 10% of the oxidizing power went to the formation of oxoacid and the balance went to gaseous products. It is now known that under their conditions and ours, any nitrite would have been converted to nitrate ion. The amount of nitrate decreased to a small fraction when enough base was added to convert ammonium ion to ammonia and to neutralize acid formed during the oxidation.

By mass spectrometer, a good yield of dinitrogen was formed when ammonia was in excess over persulfate, and negligible dioxygen was found [21].

In experiments here, an essentially quantitative yield of nitrogen was recovered (predicted: 21.5 ml, and observed: 21.2 ml; predicted: 17.2 ml, and observed: 17.5 ml) when the ammonia and persulfate reaction was carried out by a simplified gas buret. Small amounts of nitrate were detected in the ultraviolet, however, the deviations in yield from run to run were significant. A notable clue came near the end of our series of experiments when we discovered that the infinite time absorbance was about twice as large if dioxygen was mixed into the reactant solution. This point would be worth further investigation.

It is concluded that under most of the conditions of interest here the predominant reaction is:

$$3S_2O_8^{2-} + 2NH_3 \longrightarrow N_2 + 6SO_4^{2-} + 6H^+$$

and all calculations will be based on that stoichiometry.

Hydrazine Oxidation

Hydrazine N_2H_4 is a logical intermediate to consider in the oxidation of ammonia to dinitrogen (see below). As Yost *et al.* [22] found that oxidation of hydrazinium ion by persulfate in 1 M $HClO_4$ required catalysis, we checked the free base oxidation and found it to be rapid at room temperature; copious bubbling indicates the process:

$$2S_2O_8^{2-} + N_2H_4 \longrightarrow N_2 + 4HSO_4^-$$

The rates were estimated from initial slope data and integrated plots for loss of persulfate as a function of time. With excess hydrazine, the rate is first order in persulfate and first order in hydrazine. For a series of four groups of runs, we obtained average second-order rate constants of 1.64×10^{-3}, 1.71×10^{-3}, 1.57×10^{-3} and 1.59×10^{-3} M^{-1} s^{-1} at 26.5 °C.

Without question, hydrazine is oxidized rapidly enough to be considered an intermediate in the ammonia oxidation.

Ammonium Ion Oxidation

Below pH 9.3, ammonium ion is the predominant nitrogen(–III) species. Irrespective of the stoichiometric details, the reduction of persulfate generates acid and therefore the nitrogen will remain protonated throughout a run.

With ammonium ion in excess, first order plots for loss of persulfate (added as $K_2S_2O_8$) with time were linear. The reaction rate does not depend on ammonium ion concentration; in fact, the rate of persulfate loss was only slightly larger than the loss of persulfate in pure water.

Some of our data on rate of persulfate loss are as follows:

1. At 70 °C with $[S_2O_8^{2-}]$ = 0.1 M with air atmosphere, but zero ammonium ion, the first order rate constant was 2.7×10^{-5} s^{-1}.
2. Under conditions as in [1] but with 1 M ammonium ion, the constant was 3.8×10^{-5} s^{-1}.
3. Under conditions as in [1] but at 60 °C, the constant was 6.0×10^{-6} s^{-1}.
4. Under conditions as in [2] but at 60 °C, the constant was 9.8×10^{-6} s^{-1}.
5. At 70 °C with $[S_2O_8^{2-}]$ = 0.1 M with argon atmosphere but zero ammonium ion, the constant was 2.7×10^{-5} s^{-1}.
6. Under conditions as in [5] but with 1 M ammonium ion, the constant was 4.0×10^{-5} s^{-1}.

In the three pairs of experiments, the ammonium ion increased the rates by factors of 1.44, 1.64 and 1.50 fold, respectively. This enhancement is almost surely a consequence of stoichiometry. The close similarity in rate constants following the same law for the water and ammonium ion oxidations indicates that the first step in each mechanism is the same. This is further indicated by the values of activation energy, 140 ± 2 kJ mol^{-1} for water [6] and 142 kJ mol^{-1} for ammonium ion [20]; our water oxidation constants agree with literature values [4]. Given then that the first step in each oxidation is the same (homolysis of persulfate) and rate determining, it follows that the loss of persulfate in the presence of ammonium ion should go about 50% faster because three persulfate ions are needed for production of dinitrogen whereas only two are required for water oxidation (provided only that no disproportionation of intermediates such as H_2O_2 in the water oxidation occurs). Since the water oxidation is radical but non-chain, the same must be true for the ammonium ion oxidation.

Ammonia Oxidation

A number of preliminary experiments were carried out on the ammonia oxidation. While we shall not give the results of these in detail, a statement about each is needed. It was found that slightly higher rates were obtained when the ammonia was added as 'ammonium hydroxide' than when the ammonia was formed *in situ* from ammonium ion plus sodium hydroxide. It seems likely that a catalyst such as copper ion (see below) is present in bottles of ammonium hydroxide and that the lower rate more nearly represents the true rate of ammonia oxidation by persulfate. Ammonium hydroxide was not further used. The rates observed are only slightly greater than the rate of loss of persulfate in water. When the ammonia concentration was comparable to the persulfate concentration, it was found that the first order plots were non-linear with a soft sigmoid shape; since the ammonia is being converted to ammonium ion (as well as oxidation product), a slight deviation from linearity is not surprising. The rate of ammonia oxidation showed no significant dependence on the presence of oxygen or added EDTA.

Some kinetic data for the ammonia oxidation by persulfate are given in Table II. The reaction is zero order in ammonia concentration and first order in persulfate concentration so the rate law is

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_{obs}[S_2O_8^{2-}]$$

and the value of k_{obs} is about 2.1 times the value of k_1 provided sufficient ammonia for the stoichiometric need is present.

TABLE II. Rates of Ammonia Oxidation by Persulfate[a].

$[S_2O_8^{2-}]$/M	$[NH_3]$/M	$k \times 10^5/(s^{-1})$
0.011	0.11	6.0
0.011	0.22	6.0
0.011	0.55	5.8
0.011	1.09	6.2
0.11	1.09	5.8
0.11	0.75	5.8
0.11	0.50	5.3
0.11	0.275	5.5
0.11	0.25	5.8
0.11	0.125	4.3[b]
0.11	0.11	4.0[b]
0.11	0.075	3.7[b]
0.11	0.050	3.5[b]
0.11	0.025	3.3[b]

[a] At 70°, using NH_4Cl and NaOH to generate NH_3 in solution; each constant is the average from two runs. [b] For these runs where $[NH_3] \leq [S_2O_8^{2-}]$, poor first order plots were obtained.

TABLE III. Temperature Dependence of Ammonia Oxidation[a].

Temp. (°C)	k (s^{-1})
61.0	1.5×10^{-5}
65.0	2.8×10^{-5}
70.3	6.0×10^{-5}
74.5	1.18×10^{-4}

[a] At $[S_2O_8^{2-}]$ = 0.11 M and $[NH_3]$ = 1.1 M; each rate constant is the average from two runs.

A study of the temperature dependence for ammonia oxidation was carried out and the data are given in Table III. The Arrhenius plot (correlation coefficient = 0.999) gave an E_a value of 141 kJ mol^{-1}.

Again it seems certain from the results that this is a radical non-chain process which has as its rate-determining step the homolytic scission of persulfate. The proposed mechanism is:

$$S_2O_8^{2-} \xrightarrow{k_{1a}} 2SO_4^{\cdot -}$$

$$SO_4^{\cdot -} + NH_3 \xrightarrow{k_{1b}} HSO_4^- + NH_2\cdot$$

$$2NH_2\cdot \xrightarrow{k_{3b}} N_2H_4$$

$$N_2H_4 + S_2O_8^{2-} \xrightarrow{k_{4b}} N_2H_2 + 2HSO_4^-$$

$$N_2H_2 + S_2O_8^{2-} \xrightarrow{k_5} N_2 + 2HSO_4^-$$

with all steps after the first being fast.

This mechanism also predicts that the k_{obs} value for ammonia oxidation should be 1.5 times as large as the persulfate oxidation of water, whereas the observed ratio is slightly larger, being 2. We do not consider this difference a serious problem because by changing the last step of the water oxidation mechanism from 4a to 4a′ alters the predicted difference from 1.5 to 3.0.

Inspection of this mechanism indicates that the only change necessary to convert to an appropriate one for ammonium ion oxidation is to replace step k_{2b} by:

$$SO_4^{\cdot -} + NH_4^+ \xrightarrow{k_{2c}} HSO_4^- + NH_2\cdot + H^+$$

Both mechanisms invoke the same three nitrogen intermediates (amide radical $NH_2\cdot$, hydrazine, and diimide) and both give (when the steady-state approximation is used) the rate law:

$$\frac{-d[S_2O_8^{2-}]}{dt} = 3k_{1a}[S_2O_8^{2-}]$$

in agreement with experimental results.

Copper Catalysis

The fact that with ammonium hydroxide we obtained high rates was felt to be consistent with trace metal catalysis. A search of the literature showed that both ammonium ion [23] and ammonia [24] could be oxidized readily by persulfate if silver ion were present. Hall [21] found that copper ion acts as a catalyst but a rate law was not obtained.

For small amounts of added copper sulfate (up to about 4 X 10^{-5} M), the process still appeared to be first order in persulfate while the rate constant was increasing. At higher concentrations of copper(II), an induction period became noticeable and the pseudo-first-order plots after the induction period were no longer linear. A number of runs, all at 61 °C and [Cu(II)] = 4.5 X 10^{-4} M, gave linear arrays when plotted as one-half order in persulfate, see Fig. 3, which also shows the induction period; these results are strong indications of a chain reaction. A mechanism using many of the steps in the non-catalyzed process can be postulated; this is:

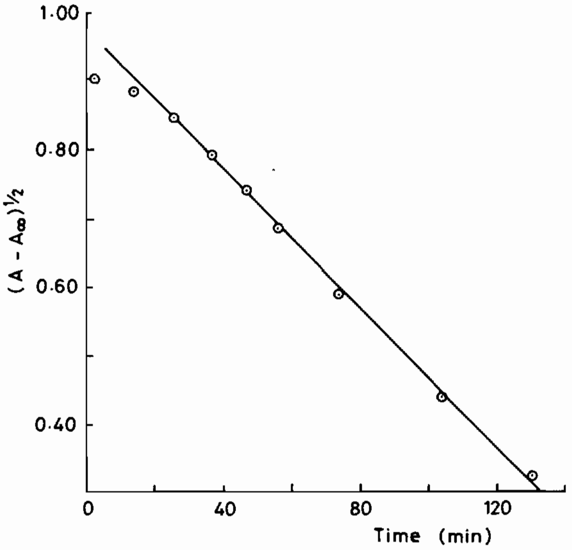


Fig. 3. A rate plot for the copper-catalyzed oxidation of ammonia by persulfate, showing the induction period and a linear display based on the integrated one-half order equation. This plot covers about 90% reaction. Conditions are 0.106 M persulfate, 053 M ammonia, 4.5 X 10^{-4} M cupric ion and 61 °C.

$$S_2O_8^{2-} \xrightarrow{k_{1a}} 2SO_4^{\cdot -}$$

$$SO_4^{\cdot -} + NH_3 \xrightarrow{k_{2b}} HSO_4^- + NH_2\cdot$$

$$NH_2\cdot + Cu(II) \xrightarrow{k_6} NH + Cu(I) + H^+$$

$$Cu(I) + S_2O_8^{2-} \xrightarrow{k_7} Cu(II) + SO_4^{2-} + SO_4^{\cdot -}$$

$$2NH_2\cdot \xrightarrow{k_{3b}} N_2H_4$$

$$S_2O_8^{2-} + N_2H_4 \xrightarrow{k_{4b}} 2HSO_4^- + N_2H_2$$

$$2NH \xrightarrow{k_8} N_2H_2$$

$$S_2O_8^{2-} + N_2H_2 \xrightarrow{k_5} 2HSO_4^- + N_2$$

The k_{1a} step is initiation, as it is in other known persulfate thermal chain oxidations. Steps 2b, 6 and 7 are propagations, and the k_{3b} dimerization now becomes the chain termination. Upon application of the steady-state approximation, we obtain the rate law:

$$\frac{-d[S_2O_8{}^{2-}]}{dt} = k_{1a}[S_2O_8{}^{2-}] + k_6\left(\frac{k_{1a}}{k_{3b}}\right)^{1/2}[S_2O_8{}^{2-}]^{1/2}[Cu(II)]$$

in agreement with the experimental results. From the data on Table IV, it is estimated that the chain length is about thirty when the copper(II) concentration is 8×10^{-4} M.

Some rates as a function of temperature are given in Table V. For the copper-catalyzed path, the Ea value is 96 kJ mol^{-1}, which should be and is less than the non-chain value.

TABLE IV. Rates of Copper-Catalyzed Ammonia Oxidation[a].

$[CuSO_4]$ M	$t_{1/2}$ min	$k_{1/2} \times 10^4$ (uncorr)	$k_{3/2}$
none	(201)[b]		
4.2×10^{-6}	212		
8.3×10^{-6}	168		
1.7×10^{-5}	134	(0.23)	(1.4)
4.2×10^{-5}	90	(0.34)	(0.8)
8.3×10^{-5}	52	0.60	0.54[c,d]
1.7×10^{-4}	28	1.11	0.60[d]
4.2×10^{-4}	12.0	2.6	0.58[d]
8.3×10^{-4}	6.3	4.9	0.52[d]

[a] At 70 °C with $[S_2O_8{}^{2-}] = 0.10$ M and $[NH_3] = 1.0$ M. Values of k were based on the averages from three runs. The values in parentheses were used for comparison purposes because of persulfate order change. [b] This is the average of nine runs with no added copper. [c] The correction for zero copper rate amounts to 24% for this run. [d] Units are $M^{-1/2}\ s^{-1}$.

There are some interesting aspects of this chain mechanism. Step k_6 is analogous (copper(II) oxidation of a radical) to that seen in copper-modified mechanisms of organic compound oxidation by peroxides. Step k_7 has been postulated previously in persulfate oxidations. Step k_{3b} (as in the non-chain cases) produces the nitrogen-nitrogen bond that is present in the dinitrogen product. Step k_{4b} as mentioned earlier is very rapid and the oxidation of diimide (step k_5) is expected to be rapid also.

No evidence for a direct displacement by ammonia as a nucleophile on the peroxide was seen. From data in Table II, we estimate that any second-order process must have a rate constant less than $3 \times 10^{-6}\ M^{-1}\ s^{-1}$ at 70 °C.

TABLE V. Temperature Dependence of Copper-Catalyzed Rate[a].

Temp. (°C)	$k_{1/2} \times 10^4$	$k_{3/2}$[b]
61.0	1.0	0.22
65.0	1.5	0.32
70.3	2.5	0.54
74.5	3.8	0.81

[a] $[S_2O_8{}^{2-}] = 0.1$ M, $[NH_3] = 1.0$ M and $[CuSO_4] = 4.2 \times 10^{-4}$ M. [b] Units are $M^{-1/2}\ s^{-1}$.

Discussion

Since mechanisms were given in the previous sections, it is not necessary to report them here. As pointed out in the Introduction, the paths for nitrogen nucleophile oxidation by persulfate are multiple and varied because of the particular combinations of reactivities for the species involved.

The order of nucleophilic reactivity of three nitrogen species on the E_n scale is aniline > nitrite > ammonia, and the second order rate constants with persulfate follow this ranking. Aniline reacts about two powers of ten faster than nitrite and nitrite in turn is at least two powers of ten faster than ammonia (for which no simple displacement could be observed). Nitrite reacts with the same rate law as bromide and with comparable rates.

In the second-order path for nitrite oxidation, we found it necessary to invoke radical participation started by an electron abstraction step:

$$S_2O_8{}^{2-} + NO_2{}^- \longrightarrow NO_2\cdot + SO_4{}^{\cdot-} + SO_4{}^{2-}$$

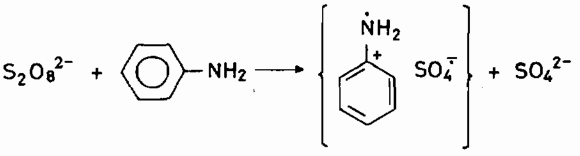
It may also be appropriate to consider electron abstraction in other persulfate and sulfate radical-ion oxidations of nitrogen compounds. For example, the second step in ammonia oxidation could be:

$$SO_4{}^{\cdot-} + NH_3 \longrightarrow SO_4{}^{2-} + NH_3{}^{\cdot+}$$

followed by

$$NH_3{}^{\cdot+} \longrightarrow NH_2\cdot + H^+$$

In the aniline oxidation, electron abstraction is conceivable as in the step:



with the radical pair in brackets collapsing to form an *ortho*-sulfate intermediate which then loses a hydrogen to become product.

It would be interesting to study the persulfate oxidations of pyridine and azide ion (E_n values of 1.20 and 1.58 respectively). Also hydrazine and hydroxylamine, both alpha-nucleophiles for which we have no E_n values, would provide worthwhile information.

One of the steps in the persulfate decomposition in water for which we need direct information is the formation of dioxygen from hydrogen peroxide. Our results with the k_1 term in nitrite oxidation indicate that it should be possible to obtain the absolute value of k_{1a} which is the rate constant for persulfate homolysis. Comparison of this value with the overall water oxidation rate will tell how the two final steps with constants k_{4a} and k'_{4a} compete as a function of pH.

Experimental

Reagents

Distilled water was deionized prior to use by passage through a Barnstead mixed bed ion exchange column. Potassium persulfate (B. + A. and Mallinckrodt Reagent) was recrystallized from distilled-deionized water to ensure maximum, but presumably not total, removal of impurity metals. Other materials —NaOH, NH_4Cl, NH_4OH, Na_2H_2EDTA, $CuSO_4$, $NaNO_2$—were the best grade available and were used without further purification. Allyl alcohol (Eastman) was distilled before use.

Equipment

Conventional laboratory spectrophotometers (*e.g.*, PE 139 and Cary 15), pH meters (L. & N. 7401) and constant temperature baths were employed.

Nitrite Procedures

Stock solutions were temperature pre-adjusted and then mixed. Aliquots were taken, cooled and absorbances read at 260, 300 and 353 nm. From extinction coefficients evaluated from Beer's law plots for the three absorbing species ($S_2O_8^{2-}$, NO_2^-, and NO_3^-) at the three wavelengths, it is possible to calculate concentrations. Sulfate and phosphates do not absorb at these wavelengths. The reaction of persulfate and allyl alcohol was followed by iodometric determination of persulfate.

Ammonia Procedures

The rate of disappearance of persulfate was monitored at ultraviolet wavelengths selected to yield optimal changes in absorbance during a run. On occasion, scans of the ultraviolet spectrum were also made, for example, to check for nitrate product. It was found that the extinction coefficients for persulfate were strongly dependent on temperature, specifically ϵ increases as temperature increases.

Buffer solutions were omitted, for under the first order conditions of excess ammonia (10x over persulfate) not even formation of acidic products could lower the NH_3 to a level comparable to persulfate. Temperatures were held constant by thermostated cell holders accurate to ±0.5 °C.

For runs in which oxygen was excluded, a mixed persulfate and ammonium salt solution was first stored in a 100 ml vessel above a syringe containing a small piece of plastic for stirring, that was previously flushed with argon. After bubbling the gas through the solution at 25 °C for ten minutes and filling the syringe with the degassed liquid, the same procedure was applied to upon a separate solution of NaOH. Next, the basic solution syringe was emptied into the persulfate solution syringe with the aid of a tube with connecting female joints. Slow forced removal of some of the contents while combining the joints reinforced the oxygen-free conditions. Matched group glass silica cells of 10 mm path length collected each reacting mixture; for runs on the PE 139 spectrometer, at least one rinsing with solution preceded the recordings.

For some rate plots, computer assisted linear regression analysis had value in fitting the experimental data to a line and in assaying slopes and correlation coefficients.

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