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The chemical reduction of nitrate in aqueous solution

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Contents

Abstract

The nitrate ion has high chemical stability, especially at low concentrations. Standard reduction potentials indicate that it should serve as an excellent oxidizing agent, but in order to react with suitable reducing agents to form elemental nitrogen or ammonia, special conditions, such as catalysts and high temperature and pressure, are required. A review of the literature on the chemical reduction of nitrate in aqueous systems has found about a

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hundred articles dealing with nitrate removal from such systems, with the majority having been published over the last decade. The reducing agents which have been examined to the greatest extent for acidic solution are formic acid, iron metal, methanol and the ammonium ion; while for basic solution aluminum, zinc and iron metals, iron(II), ammonia, hydrazine, glucose and hydrogen have been studied.

Keywords: Nitrate; Nitrite; Ammonia; Chemical reduction; Nitrogen; Aqueous solution

1. Introduction

The nitrate ion, with nitrogen in the +5 oxidation state, is found in a wide variety of aqueous solutions and mixtures. In most of these, the reduction of the nitrate plays an important role in the overall chemistry of these composites, even though the ion might be present at very low concentrations. This review is to examine the chemical reduction of nitrate in such media, the reducing agents used and the conditions employed.

The chemistry of the nitrate ion is often described in basic texts with only a brief mention since below 2 M the ion is difficult to reduce [1]. Also, in such solutions, nitrate is a very weak base; behaves as a poor ligand, even though metal nitrate complexes are well-known [2]; and does not form highly insoluble precipitates with common metal ions. However, the chemistry of nitrate is far from being unexciting since it presents some major challenges to scientists and engineers in their attempts to carry out reactions with it.

Described below are six systems in which nitrate, dissolved in aqueous media, is important and where its reduction chemistry is significant. In each case reducing it to one or more nitrogen species of lower oxidation state, primarily NO_2^-, N_2O, N_2 and NH_3 destroys the nitrate ion. Studies on each of these systems have examined and employed a variety of chemical reducing agents to accomplish nitrate reduction. This review will cover the recent work and point out the different types of reducing agents that have been used in these studies.

1. Drinking water supplies—much of the nation's drinking water, especially that coming from groundwater, is at risk from nitrate contamination [3]. The sources of this contamination include fertilizers, animal manure and atmospheric deposition from nitrogen oxide emission [4–6]. Traces of nitrate in drinking water may lead to methemeglobmenia in infants, and with long-term exposure is a possible cancer risk. There is a major effort to keep the nitrate concentration in drinking water below the US Environmental Protection Agency maximum containment level of 10 mg nitrate nitrogen l^{-1}. The removal of nitrate from drinking water presents a challenge because of the ion's high stability and soluble nature [7]. A number of treatment technologies have been used, but ion exchange, reverse osmosis and biological denitrification have been applied full-scale. As will be described in this review chemical reductants have also been examined to a limited extent.

2. Nuclear waste—a large amount of nitrate containing aqueous mixed (radioactive and Resource Conservation and Recovery Act (RCRA) hazard) wastes of all types are stored at various US Department of Energy (DOE) facilities. The wastes have high concentrations of nitrate salts or nitric acid, and if solidified, the nitrates will add significantly to the storage volume and affect the integrity of the solid waste form. If the wastes are to be processed at high temperature, the nitrate will interfere with the chemistry under those conditions and lead to the possible generation of pollutant gases such as NO_x. Therefore, it is important to remove a significant portion, or all, of the nitrate from the waste. Taylor et al. [8] have evaluated the nitrate destruction methods that have been proposed for nuclear waste treatment. They describe in some detail the following processes: the nitrate to ammonia and ceramic (NAC); electrochemical destruction; biological denitrification; chemical reduction; hydrothermal; and calcination. All but the biological denitrification process will be discussed below. At the time of the report no process was found to be the ‘best’, and it was recommended that more work be done on the nitrate destruction problem.
3. Analytical procedures—the older methods for nitrate determination in water, prior to such techniques as ion chromatography, involved chemically reducing the trace amount of nitrate present to ammonia which would be distilled into a known volume of standard acid for analysis [9], or, the nitrate would be reduced to nitrite, and then be diazotized to an intensely colored azo-compound whose color intensity would be measured spectrophotometrically. A number of reducing agents have been proposed for the many methods available [6].
4. Models for biological-denitrifying systems—there has been considerable interest over the years to determine how certain biological systems utilize nitrate and nitrite nitrogen to produce ammonia. This interest has created an enormous amount of literature, some of which describes the use of inorganic model compounds to catalyze the reduction of the oxynitrogen species to lower oxidation states of nitrogen. Studies of this type have provided oxynitrogen anion reduction mechanisms to be proposed [10,11].
5. Origin of ammonia on early earth—a non-reducing atmosphere existed on the earth prior to life formation. Chemical models are being developed to determine how ammonia resulted from nitrate under these conditions, which involves nitrate reduction in aqueous solution using reducing species found in minerals [12]. The ammonia would eventually lead to the formation of amines and amino acids.
6. Generation of some valuable, relatively expensive compounds—the controlled reduction of nitrate may eventually produce such compounds as N_2O, N_2H_4, and NH_3 that are now generated at high cost [13].

The chemical reduction of nitrate does occur in media other than aqueous ones, such as in pyrotechnic and explosive materials. Many of these materials are formulated with nitrate and a reducing agent, e.g. NH_4NO_3 [14,15]. Even though the reaction takes place in the solid state at high temperature, the nitrate is chemically reduced, and some aspects of such reactions apply to aqueous solution.

Below are listed, in alphabetical order, seven types of nitrate reducing agents. After which a section on reduction using energy sources is included. There are three ways to reduce nitrate using energy sources: electrochemical, photochemical and thermal. Since they are closely related to the chemical methods, some mention of them was necessary. The literature of the electrochemical and photochemical methods is large and only a few pertinent references are given here. Recent citations should provide a more complete list of references.

A list of some of the reducing agents treated in this review are shown in Table 1 along with their reduction potentials in acid and base solution. Also shown below the table are the potential diagrams relating the various nitrogen species found in acid and base solution.

The literature over the past ten years has been examined in detail, and earlier articles of special note are included. There have been a large number of articles published in recent years, primarily on water purification (1) and nuclear waste (2). A minimum of government documents are being referenced since they are difficult to access, usually have not been refereed and often deal more with the engineering aspects of nitrate destruction rather than detailed chemistry. Much of the work described in these documents has been published in the chemical literature.

2. Chemical reducing agents

2.1. Active metals

Active metals have been used in various analytical procedures for many years to reduce nitrate in basic solution to nitrite or ammonia. Most procedures describe adding the active metal to a highly basic solution with a small nitrate concentration. Some of the metals that have been suggested for analytical use are: Cd [16]; Cd amalgam [17,18]; Al [9]; Devarda's alloy (50Cu, 45Al, 5Zn) [6,9]; Zn [19]; and Arndt's alloy (60 Mg, 40Cu) [9]. New water purification methods and processes to reduce nitrate in radioactive and hazardous wastes using active metals are being developed.

Water containing small amounts (ca. 1 mM) of nitrate may be purified with Al powder [20]. At pH values less than 8, no nitrate or sulfate reduction takes place when the powder is added, but at values greater than 11.5 both are reduced, while at pH 10.5 only nitrate is reduced. Ammonia is the principal product with some nitrite and nitrogen gas:

$$3NO_3^- + 2Al + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3$$

$$NO_2^- + 2Al + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^-$$

$$2NO_2^- + 2Al + 4H_2O \rightarrow N_2 + 2Al(OH)_3 + 2OH^-$$

The precise nature of the Al product was not identified, but the concentration of Al^{3+} in solution after reduction was reported to be < 1 μM.

Aluminum powder has been suggested for use in reducing nitrate in sodium-based nuclear wastes employing the NAC process [21,22]. The powder is added to a highly basic solution (pH > 11.5) which has a nitrate concentration of about 4 M and is at a temperature of 50°C. A vigorous reaction takes place that has to be carefully controlled. The calculated heat of reaction for the reduction of nitrate to ammonia and the conversion of Al metal to oxide is -1595 kJ mol^{-1} of $NaNO_3$. The possibility of generating hydrogen gas exists, but this has not been a significant problem with careful control of the reaction conditions:

Table 1
Some of the nitrate reducing agents discussed in the review

Reducing agent	E° [a] (V)	Acid (A) or base (B)	Use [b]	N products [c]	Other products	Conditions [d]
Al (s)	-2.30	B	L, H	NH_3, NO_2^-, N_2	$Al(OH)_3$, H_2	
Fe(s)	-0.037	A	L	NO_2^-	Fe^{3+}	
	-0.771	B	L	N_2	Fe_2O_3, OH^-	
Zn	-1.245	B	L	NO_2^-, NH_3, N_2	$Zn(OH)_2$?	? Cat
NH_4^+	$+0.27$ (N_2)	A	L	N_2O, N_2		hi T&P, Cl^-
NH_3	-0.74 (N_2)	B	L	N_2, NO_2^-	OH^-	hi T&P
BH_4^-	-1.24	B	H	NO_2^-, NH_3	$B(OH)_4^-$, H_2	Cu(II)
HCO_2H	-0.199	A	H	N_2O, NH_3	CO_2	Rh/C
		A	H	N_2	CO_2, H_2	hi T&P
CH_3OH	$+0.017$(CO_2)	A	H	NH_4^+	HCO_3^-	hi T&P
NH_3OH^+	-0.05	A	L	N_2O		
NH_2OH	-1.05	B	L	N_2O	OH^-	Cu(II)
H_2	-0.828	B	L	N_2	OH^-	Cu–Pd
Fe(II)	$+0.771$	A	L	NO, N_2O, N_2	Fe^{3+}	
	-0.56	B	L	NH_3	$Fe(OH)_3$, OH^-	Cu(II), Ag(I)

[a] The standard reduction potential, E°, values are from Refs. [100–102]. If there is any question regarding the other half of the redox couple involved, then it is shown in parentheses.

[b] The use column shows whether the agent has been used primarily in dilute nitrate solutions (L) or concentrated (H) ones.

[c] The primary nitrogen products mentioned in the review are given in addition to other important products.

[d] Some special conditions are shown. The term 'hi T&P' represents exceptionally high temperature and pressure being used.

Acid

$$NO_3^- \xrightarrow{0.803} N_2O_4 \xrightarrow{1.07} HNO_2 \xrightarrow{0.996} NO \xrightarrow{1.59} N_2O \xrightarrow{1.77} N_2 \xrightarrow{-1.87} NH_3OH^+ \xrightarrow{1.41} N_2H_5^+ \xrightarrow{1.275} NH_4^+$$

$$NO_3^- \xrightarrow{0.875} NH_4^+ \quad NO_3^- \xrightarrow{1.246} N_2$$

Base

$$NO_3^- \xrightarrow{-0.86} N_2O_4 \xrightarrow{0.867} NO_2^- \xrightarrow{0.46} NO \xrightarrow{0.76} N_2O \xrightarrow{0.94} N_2 \xrightarrow{-3.04} NH_2OH \xrightarrow{0.73} N_2H_4 \xrightarrow{0.1} NH_3$$

$$NO_3^- \xrightarrow{-0.01} NH_3 \quad NO_3^- \xrightarrow{0.43} N_2$$

$$2Al + 6H_2O \rightarrow 3H_2 + 6OH^- + 2Al^{3+}$$

The $Al(OH)_3$ product is gibbsite, $Al_2O_3{\cdot}3H_2O$, which appears after the solution is saturated with the soluble aluminate ion, AlO_2^-. A considerable amount of engineering study has gone into attempts to make the NAC process a viable one for use in treating nuclear waste [23].

The reduction of inorganic and organic nitrates in aqueous solution in the presence of Al results in nitrite, ammonium derivatives and ammonia according to Lur'e et al. [24]. The Al reaction involves a competition between the surface passivation with the formation of boehmite, $Al_2O_3{\cdot}H_2O$, and the dissolution of the protective boehmite layer in the alkaline medium to form the aluminate ion. The nitrate ion tends to dissolve the passivated surface of Al due to the increased alkalinity from the formation of nitrite.

A water purification process using copper-coated Fe powder to treat neutral solutions containing nitrate has been described [25]. The ion is reduced to the ammonium ion via the nitrite ion. As part of a study on removing a banned nematicide 1,2-dibromo-3-chloropropane, from water, Fe powder was found to react rapidly with nitrate to produce nitrogen gas and nitrite [26].

$$10Fe + 6NO_3^- + 3H_2O \rightarrow 5Fe_2O_3 + 6OH^- + 3N_2$$

$$Fe + NO_3^- + 2H^+ \rightarrow Fe^{3+} + H_2O + NO_2^-$$

Earlier it had been reported that Fe powder was not an economically attractive chemical reduction method for water purification [27].

Till and co-workers [28] have shown that Fe metal can be used as a continuous source of cathodic hydrogen for biological denitrification as well as a direct reductant of nitrate. The metal may react with water in pH range 6–9 to produce hydrogen which is then used in autotrophic denitrification by *Paracoccus denitrificans* as an electron donor with nitrate being converted to N_2 and microbial growth taking place. Steel wool is useful for the denitrification, while Fe powder results primarily in the chemical reduction of nitrate to ammonia.

A patent has recently been described which employs Zn for a low temperature treatment of wastewater containing nitrate [29]. Nitrogen gas, ammonia and nitrite result; however, if an undisclosed catalyst is present only nitrogen gas is formed (see Section 2.2).

The use of Devarda's alloy for nitrate reduction has been examined with open circuit potentials measured at the alloy electrode [30]. The reduction occurred at pH values greater than 11 with an induction period that decreased as the pH increased. The ammonium ion formed from the nitrate through the nitrite due to a local cell reaction on the alloy surface. The potential shifted abruptly to a more negative potential with an induction period at a $pH > 10.3$. The results indicate a destruction of the passivation film on the alloy in the alkaline solution.

In order to understand the denitrification or the dissimilatory enzymatic reduction of nitrate and nitrite to NO, N_2O, and/or N_2 gases, a number of model compounds have been prepared and reacted with the oxynitrogen ions. Many of these compounds are metal complexes and their study has allowed for possible mechanisms to be proposed for the role of metals in the biochemical reduction process. The kinetics study of the reaction of a dimeric aquamolybdenum(III) complex with nitrate provided direct evidence for an oxo-group transfer from the nitrate to the metal to oxidize the metal and form nitrite [31]. A nitrate reductase analog reaction system was developed and examined using a Mo(IV) complex and its reaction with nitrate [32]. From this, atom transfer appears to be a plausible pathway in the mechanism of nitrate reductases. These types of studies have been extended recently to copper complexes and their reaction with nitrite to form NO [11,33,34].

2.2. Ammonia

The reduction of nitrate with ammonia in base solution or ammonium in acid solution to nitrogen and/or nitrous oxide is expected, based on the standard redox potentials and such reactions do occur; but only at high temperatures and pressures. Such a reaction takes place when ammonium nitrate explodes at high temperature and pressure [14,15]. The heating of aqueous solutions of ammonium nitrite under atmospheric conditions produces nitrogen [35]:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

Small amounts of nitric oxide and nitric acid are also formed.

In a study of the reaction of six reducing agents, including ammonia, with 3% (w/w) nitrate at pH 13, 200–350°C and 40–200 atm, ammonia was found to be very poor compared to formate, glucose, urea, and hydrogen and was about equal to methane [36]. Ammonia was a much better reducing agent under acidic conditions than basic conditions. N_2 was the primary product under both conditions:

$$5NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 2H^+ + 9H_2O$$

$$5NH_3 + 3NO_2^- \rightarrow 4N_2 + 3OH^- + 6H_2O$$

Some N_2O was also produced.

Dell'Orco and co-workers [37–39] have carried out extensive studies on the destruction of nitrates with ammonia by hydrothermal processing. For example, the reaction of nitrate and ammonium ions is complete in less than 30 s at 374.0°C and 218 atm, the critical point of water, producing nitrogen and nitrous oxide. This reaction has been carried out in supercritical water (300 atm, 450–530°C) with no organic matter present over the following ranges: $[NO_3^-]$ 6.86–10.3 mM; $[NH_3]$ 7.11–10.28 mM; and pH 2.8–10.5. The reaction products under these conditions also included nitrite, which was important at high pH. Maximum destruction of nitrate occurred at low pH values. A mechanism for the reaction has been developed which initially involves the formation of NO_2 and NO by hydrolysis and homolysis pathways; followed by the reaction of these species with the radical, $^{\bullet}NH_2$, formed by the hydrogen abstraction from ammonia, to produce the observed reaction products, N_2 and N_2O. This study showed that NO might be produced when nitrates and nitrites are present without excess oxygen.

Solutions containing NH_4NO_3 (20%, w/w), heated to 180°C in a pressure reactor, formed nitrous oxide and nitrogen in a 4:1 ratio [40]. Chloride was present at a concentration of about 0.1 M and the $[H^+]$ was about 0.2 M. The nitrous oxide:nitrogen ratio increased as the acid concentration increased. If chloride ions were not present, no reaction took place. Kinetics and isotopic labeling experiments have indicated that NO_2Cl is an intermediate in the reaction. A mechanism has been proposed for the decomposition which shows the nitrosonium ion NO_2^+, reacting with the chloride ion to produce NO_2Cl. If NH_4^+ reacts with NO_2Cl, N_2O is formed after several steps; while N_2 is formed when NH_3 reacts with NO_2Cl.

A process involving the reduction of nitrite with ammonia has been described in a recent patent [29]. Nitrate-containing wastewater is treated with metals, such as zinc, to form nitrite ions, which are reacted with ammonia in the presence of a catalyst to form N_2. The resulting metal ions are removed by a softening treatment (see Section 2.1).

2.3. Borohydride

Sodium borohydride, or sodium tetrahydridoborate, serves as a reducing agent for many reactions [41], but it does not reduce nitrate in acid solution [42]. A spectrophotometric method for the determination of nitrate in water has been reported which has $NaBH_4$ reacting with nitrate in the presence of a Cu/Zn alloy [43]. Solutions containing 1 M $NaNO_3$/1 M NaOH have been found to react with $NaBH_4$ at 65°C in the presence of Cu^{2+} ions to form initially nitrite, and then ammonia, in addition to free Cu and Cu_2O and some H_2 [44].

Nitrite does react with BH_4^- in the presence of acid to form NH_4^+ [42]. The kinetics and mechanism of the acid-catalyzed amine-borane, $(CH_3)_3NBH_3$, reduction of nitrite to produce the amine salt, N_2O and H_2 has been studied [45].

$$(CH_3)_3NBH_3 + 2HNO_2 + H_3O^+$$

$$\rightarrow (CH_3)_3NH^+ + B(OH)_3 + N_2O + H_2 + H_2O$$

2.4. Formate and other organic species

Formic acid is being used to treat high level nuclear waste (HLW) that is to be vitrified. The acid not only reduces nitrate, but it also affects glass redox chemistry and melter feed rheology control, and reduces any Hg present in the metallic form. Because of this, considerable study has been focused recently on the reaction of formate with nitrate and nitrite; however earlier studies showed that the reaction of nitric acid and formic acid in concentrated sulfuric acid provided an interesting example of an oscillatory reaction [46]. A mixture of concentrated sulfuric, concentrated nitric, and formic acids in a 5:1:1 ratio, when heated to 50°C in a closed system, gave periodic variations in the gas (primarily CO_2, NO_2, and CO) pressure that develops, in the color (faint blue) of the mixture, and in the amount of foam. To account for the products the reaction steps below were proposed.

$$HCOOH + HNO_3 \rightarrow HNO_2 + CO_2 + H_2O$$

$$2HNO_2 \Leftrightarrow N_2O_3(aq.) + H_2O$$

$$N_2O_3 \rightarrow NO + NO_2$$

$$N_2O_3(aq.) + 3H_2SO_4 \rightarrow 2NO^+ + H_3O^+ + 3HSO_4^-$$

$$NO^+ + H_2O \rightarrow HNO_2 + H^+$$

The source of the CO was not mentioned, but may arise from the dehydration of formic acid. The color is thought to be due to a nitroso compound formed from traces of organic impurities.

Periodic oscillations were observed in a denitration study when formic acid was reacted with simulated HLW which was ca. 5 M HNO_3 and contained a variety of metal ions [47]. Oscillations were observed in the partial pressures of NO, N_2O, and CO_2 after about 70 min of dosing with formic acid and continued for several minutes after the dosing ceased. The oscillations were affected by the presence of Pd(II).

The mechanism of the reaction of nitrate and formate is complex. An early study of the reaction in sulfuric acid (0.1–6 M) and perchloric acid (1–6 M) showed that no reaction would take place unless nitrous acid was present [48,49]. Under these conditions apparently the NO^+ species is required to form in order to have a reaction take place. Kubota and co-workers [50] found that the addition of nitrite to HLW in nitric acid solution before denitration with organic reductants lowered the induction period for the reaction to almost zero. The maximum gas evolution rate was reduced to less than 60% of that obtained in the absence of nitrite.

Dworschak and co-workers [51] have pointed out that Eq. (1), where the formic acid is in excess and the acidity is low, is highly exothermic with an induction period and a large rate of reaction.

$$2HNO_3 + 4HCOOH \rightarrow N_2O + 4CO_2 + 5H_2O \tag{1}$$

This indicates an autocatalytic mechanism that is typical for a runaway reaction and represents a potential hazard.

They studied the addition of 3 M HNO_3 solutions to formic acid solutions and developed a mechanism for these conditions.

$$HNO_2 + HCOOH \rightarrow HNO + CO_2 + H_2O$$

$$HNO_2 + HCOOH \rightarrow {}^{\bullet}NO + {}^{\bullet}COOH + H_2O$$

$$HNO + {}^{\bullet}NO \rightarrow N_2O + {}^{\bullet}OH \tag{2}$$

$$2{}^{\bullet}OH + 2HCOOH \rightarrow 2{}^{\bullet}COOH + 2H_2O$$

$$2{}^{\bullet}COOH + 2HNO_3 \rightarrow 2HNO_2 + 2CO_2 + 2{}^{\bullet}OH \tag{3}$$

$$HNO_2 + {}^{\bullet}COOH \rightarrow {}^{\bullet}NO + CO_2 + H_2O$$

$${}^{\bullet}OH + {}^{\bullet}NO \rightarrow HNO_2$$

The sum of these equations is the overall Eq. (1). Eqs. (2) and (3) produce the hydroxyl radical, $^{\bullet}OH$, which is known to be an efficient intermediate in many chain reactions. NO was the only intermediate observed. The following reaction may also take place when excess reductant is present.

$$2HNO \rightarrow N_2O + H_2O$$

Their study showed that nitrous acid is an indispensable initiator and an intermediate in the nitric acid/formic acid reaction. Oscillations with an intermittent cessation of the reaction and a violent restart can be avoided by keeping the nitrous acid concentration high and may be produced by:

$$HNO_3 + HNO \rightarrow 2HNO_2$$

The addition of formic acid to a nitrate solution causes a decrease in the pH and a reduction of nitrate to nitrite, and then nitrite to nitrogen oxides. Mathematical equations relating the pH and redox potential to various compositions of formic acid and nitrate and nitrite have been developed [52]. Such equations may provide a way to monitor the progress of the reduction and the conditions at which the nitrogen oxides are released in the complex nuclear waste mixtures. These mixtures contain heavy metal ions that may catalyze the reaction of nitrate and formate.

Ammonia was formed when formic acid reacted with simulant waste that was 2.7 M $NO_3^-$and 0.44 M NO_2^- and contained Al, Cd, Fe, Mn, Nd, Si, Zr, Na, and carbonate ions with a supported catalyst, 5% Rh on C, present [53]. The final pH of the solution measured 6.9, a higher value than expected. The following reaction appears to be taking place:

$$5HCOOH + NO_3^- \rightarrow NH_3 + HCO_2^- + 4CO_2 + 3H_2O$$

Since 5% Rh on Al_2O_3 was a poorer catalyst and $RhCl_3 \cdot H_2O$ dissolved in solution produced no ammonia, the form of Rh is an important consideration for the reaction. Formic acid decomposes when heated to produce CO_2 and H_2. The catalyst must activate the hydrogen from the formic acid to react with the nitrate ion to form ammonia.

$$NO_3^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^-$$

The more ammonia that forms the less H_2 gas released as a final product (see Section 2.4). Pd(II) is a much less active catalyst than Rh and takes the nitrate to N_2O as well as ammonia. No nitrogen oxides were observed when nitrite free simulant is used, indicating that Rh cannot catalyze the reaction of HCOOH and NO_3^- to N_2O or NO. No mention was made in this study of any oscillatory character to the catalyzed reaction.

Reductions of halo- and nitroaromatic compounds have been carried out with a Pd–C catalyst using formate as a hydrogen transfer reagent [54]. In the presence of a catalyst the reducing action of formate and formic acid on nitrate may take place by such a mechanism. There may be several mechanisms for the reaction depending on conditions.

Formate reacts with nitrate to form N_2 under both acid and basic conditions at high temperature and pressure [36]. When a 3:1 mole ratio mixture of formate and nitrate at pH 3.9 is heated for 2 h at 350°C and 194 atm, 100% conversion of the nitrate to N_2 occurred. A 99% conversion was found when a similar mixture at pH 13.2 was subjected to 325°C and 134 atm for 2 h. The reactions for acid and basic conditions are:

$$5HCOOH + 2H^+ + 2NO_3^- \rightarrow 5CO_2 + N_2 + 6H_2O$$

$$5HCOO^- + 2NO_3^- \rightarrow N_2 + 3HCO_3^- + 2CO_3^{2-} + H_2O$$

The composition of the gas mixture was observed as a function of time for the pH 3.9 experiment and CO, H_2 and CO_2 were formed in the initial stages of the reaction from the thermal decomposition of HCOOH. As the reaction continues, water and carbon monoxide reacted to produce a maximum amount of CO_2 and H_2 and the rate of N_2 production increased.

The use of formic acid has been evaluated as a nitrate destruction method for nuclear waste [8]. Even though it is being used in several countries it has not been recommended for use in the US.

In the treatment of HLW, oxalic acid may be added to formic acid in order to have substantial partitioning of actinides and rare earths from fission products. Therefore, the reaction of oxalic acid with nitric acid was carried out, and it was found that it reacted like formic acid; in fact, it appeared to be even more reactive than formic acid [51]. The oxalic acid study provided further information on the formic acid mechanism and showed that with Fe and Cu metal ions present the oxalic acid is 'protected' from the reaction, probably by complex ion formation.

A number of simple organic compounds have been used, or attempts have been made, to reduce nitrate in aqueous solutions. These include acetaldehyde, formaldehyde, glucose, methane, methanol, oxalic acid, tributylphosphate, and urea. Glucose was possibly one of the best to react with nitrate, especially at high temperature and pressure [36]. With a glucose:nitrate ratio of 0.4, a temperature of 350°C, a pressure of 158 atm, and a pH 13, 48% of the nitrate was converted to N_2 and the pH decreased to 8.2 after 2 h:

$$5/3C_6H_{12}O_6 + 2OH^- + 8NO_3^- \rightarrow 10HCO_3^- + 6H_2O + 4N_2$$

Under similar conditions, urea showed only ca. 20% conversion and methane ca. 6%. Glucose has only a small effect on nitrate in drinking water at ambient conditions, while urea and formaldehyde are ineffective [27]. Since glucose may serve as an energy source for microbial denitrification, both chemical and microbial processes may take place when it is being used [55].

Reactions of nitric acid with tributylphosphate [56] and with acetaldehyde [57] have been found.

A new direction for the reactions of organic matter with nitrate is with photochemically induced redox reactions. The nitrate ion acts as a primary chromophore and is a possible source of the highly reactive hydroxyl radical and NO. The NO_3^-/NO_2^- couple is influenced by light and organic matter. Therefore, the rate of photochemical production of NO_2^- depends on the concentration of organic matter in both deionized water and seawater [58]. Oxygen species have been formed by photoinduction from NO_3^- and they react with humic acid in water [59] (see Section 3.2).

The reaction of methanol with nitrate in nuclear waste has been carried out at 450–525°C and 300 atm [39]. The primary reaction, which rapidly takes place, is:

$$3NO_3^- + 4CH_3OH + 2H^+ \rightarrow 3NH_4^+ + 4HCO_3^- + H_2O$$

2.5. Hydrazine and hydroxylamine

Hydrazine has been used in several spectrophotometric analytical methods to reduce nitrate to nitrite. In most instances traces of a Cu(II) salt are added as a catalyst [6,60–62].

A concentrated aqueous solution of hydroxylamine nitrate (HAN) mixed with alkylammonium nitrate salts burns very rapidly, partially reducing the nitrate present. A study of the decomposition of HAN in aqueous solution has been carried out [63,64]. The reaction which occurs is:

$$4[NH_3OH]NO_3 \rightarrow 3N_2O + 7H_2O + 2HNO_3$$

However, the precise stoichiometry will vary depending on the reaction conditions and, in some cases, small amounts of O_2 are produced. The kinetics of the fast reaction has been studied in considerable detail using flow-cell IR spectroscopy. The loss of $(NH_3OH)^+$ and the formation of N_2O occur at the same rate following first-order kinetics with an activation energy of 103 kJ mol^{-1}. The pathway of the decomposition of HAN appears to involve the following steps where both HNO_3 and HNO_2 competitively oxidize NH_2OH:

$$NH_3OH^+ + NO_3^- \Leftrightarrow NH_2OH + HNO_3 \quad \text{equilibrium, } K = k_1/k_{-1}$$

$$NH_2OH + HNO_3 \rightarrow HNO_2 + H_2O + HNO \quad k_2$$

$$2HNO \rightarrow N_2O + H_2O \quad k_3$$

$$2(NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O) \quad k_4$$

A steady-state treatment of the above produces the following rate equation:

$$-\mathrm{d}[NH_3OH^+]/\mathrm{d}t = (2k_1k_2/(k_{-1} + 2k_2))[NH_3OH^+][NO_3^-]$$

2.6. Hydrogen

A method to remove nitrate from groundwater by hydrogenation has been developed recently [65,66]. A typical procedure involves placing the nitrate-containing water in a 2 l, isothermal, semi-batch, slurry reactor along with a suitable catalyst. The mixture is subjected to a H_2 pressure of about 0.4 atm, the atmosphere is made up to 1.0 atm with N_2 or CO_2 and stirred for ca. 100–300 min. Nitrogen gas, ammonia, and/or nitrite may form with an increase in the pH. Hydroxide ion formation maintains electroneutrality in the solution.

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^-$$

The best catalyst for nitrate reduction to nitrogen has been found to be a Cu(5%)–Pd(1.25%) bimetallic catalyst supported on γ-Al_2O_3 [67]. This catalyst insures that no nitrite results and a minimum of ammonia forms.

By changing such conditions as the gas mixture and the cations present, the final product mixture will vary and the time required for the reaction may change. For example, if CO_2 is used in the gas mixture the pH varies only slightly and if Al^{3+} is present the reaction is over in about 45 min. The rate-controlling step of the reaction is the irreversible bimolecular surface reaction between the reactants [66].

A problem with most chemical reduction methods for nitrate is that the chemical reaction leaves by-products other than the reduced nitrogen species. Hydrogenation forms hydroxide ion as the by-product, which is easily dealt with using CO_2, if necessary.

In the Cox et al. [36] study of the thermochemical nitrate destruction by a variety of reducing agents, H_2, with no catalyst present, achieved 18% reduction. The experiment was carried out with a 3.7:1 ratio of H_2:NO_3^-. A batch reactor was used at 360°C, 211 atm, and pH 13.2. One reason given for the low reduction percentage was the low solubility of the gaseous reducing agent in the reaction medium.

2.7. Iron(II)

Studies with Fe(II) as a nitrate reductant have been carried out for three reasons.

1. Boring profiles on certain types of soil samples have shown that nitrate concentrations decrease markedly with depth and are negligible just a few centimeters below the surface [68]. At these depths ammonia and Fe(II) become prevalent.
2. In 1976 the only practical method for removal of nitrate from water was by biological denitrification. It was possible that Fe(II) might provide an alternative method [69].
3. Theories of life require that reduced nitrogen-containing compounds be available on the ‘early’ earth. One way this might have occurred is by having high concentrations of Fe(II) in the ‘early’ oceans to reduce nitrate [12].

Iron(II) reduces nitrate in basic solution and nitrite in both acidic and basic solutions (see review by Fanning [70]). Szabo and Bartha [71–73] examined the reducibility of nitrate with Fe(II) in base solution in order to develop a new analytical method for determining nitrate.

$$NO_3^- + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + OH^-$$

They found the reaction to be influenced by Ag(I) and Cu(II). Fine colloidal particles of the free metal were initially formed that appeared to catalyze the reduction process.

The rate of the uncatalyzed reaction of Fe(II) with nitrate in basic solution to quantitatively produce ammonia was found to be much slower than that of nitrite with Fe(II) under the same conditions [74]. The effect of Ag(I) on the reaction was significant. The uncatalyzed rate of nitrate reduction in a nitrogen atmosphere at 75°C was found to be at a maximum at ca. pH 8, but the rate and the pH decreased as the reaction proceeded [75]. An explanation for this is that the reducing agent is a colloidal $(\mathrm{Fe(OH)_2})_m \cdot n\mathrm{H}^+$ and is more positively charged than the product, $(\mathrm{Fe(OH)_3})_q \cdot r\mathrm{H}^+$ .causing the formation of more H^+ as the reaction occurs.

A detailed study of the Cu(II) catalyzed reaction of nitrate and Fe(II) at 26°C under a He atmosphere from pH 6 to 10 found that maximum reduction (93%) and maximum gas production occurred at pH 8 [69]. The solution used had 25 ppm nitrate, an Fe(II):nitrate mole ratio of 12 and about 10 ppm Cu(II), producing N_2 and N_2O from 61% of the original nitrate present. The N_2O:N_2 ratio decreased as the Cu(II) level increased from 1 to 10 ppm. There was evidence for the formation, not only of N_2 and N_2O, but also for NO_2^-, NH_4^+, NH_3 and NO. The $\mathrm{Fe(OH)_2}$ formed by precipitating Fe(II) in the presence of MgO is more reactive than that formed in the presence of NaOH indicating that the structure of the reducing agent is an important factor.

In anoxic soils and sediments greenish Fe(II, III) hydroxides, known as green rusts (GR), have been reported [12]. An example of this type of compound, $[\mathrm{Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 \cdot \mathit{y}H_2O}]$, was prepared and reacted with nitrate at 25°C and pH 8.25 [76]. The reaction quantitatively produced ammonium and magnetite ($\mathrm{Fe_3O_4}$) with a rate expression of:

$$\mathrm{d[NH_4^+]/d}t = k\mathrm{[Fe(II)]_{GR}[NO_3^-]} \quad \text{where } k = 4.93 \times 10^{-5}\ \mathrm{l\ mol^{-1}s^{-1}}$$

$$\mathrm{Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4(s) + 0.25NO_3^- + 1.5OH^-}$$
$$\mathrm{\rightarrow SO_4^{2-} + 0.25NH_4^+ + 2Fe_3O_4(s) + 6.25H_2O}$$

GR have to be considered important for nitrate reduction in subsoils, sediments and aquifers where microbially mediated reduction rates are small.

In strong acid solution Fe(II) does not reduce nitrate, but does react with nitrite to produce NO and the brown, $\mathrm{Fe(NO)^{2+}}$ complex [70]. However, Wullstein and Gilmour [77] showed that the reaction of KNO_2 and $FeSO_4$ at 29°C and pH 3 and 6 under a He atmosphere produced 13–15% N_2 and no NO. Thus, it is possible that enzymes do not form all of the nitrogen produced in denitrifying systems, metal complexes may form some. However, Chalamet [78] has studied the reaction in more detail at pH 5 and found NO and N_2O were produced along with N_2.

The reaction of Fe(II) with nitrite over the pH range 6–8 in a helium atmosphere at 26°C has been shown to be slightly influenced by traces of Cu(II) [79]. N_2O was the principal product, but N_2 and NH_4^+ were also produced. The rate of production of three products was rapid and quantitative at pH 8. An increase in the amount of Cu(II) decreased the mole ratio of N_2O to N_2. Reduction of nitrite at pH 6 was incomplete, but was favored by Cu(II) addition with N_2O being the dominant product with a small amount of NO being produced. At pH 8 most of the N_2O present is reduced to N_2 with Cu(II) present; however, with no Cu(II), N_2O is not reduced.

3. Reduction using energy sources

3.1. Electrochemical

The reduction of nitrate in an electrochemical cell can be carried out under acidic, neutral and basic conditions. Most of the recent research effort in this area has centered on basic solution reduction, primarily with the expectation that this might provide an acceptable method to reduce the large amount of nitrate found in nuclear waste. Considering electrode potentials (Table 1) reduction in acidic solution takes place at more positive potentials and is, thus, more favorable in that case than in basic solution. To improve the situation for basic solutions the constitution of the cathode has had to be examined thoroughly. Determining the best material to use for the cathode and examining modifications of its surface with a bound catalyst have been two directions for these investigations.

Nitrogen oxyanions were reduced in 1 M NaOH using Ag, Cu and $CuInSe_2$ electrodes [80]. Cu was found to be the best. Nitrate was reduced on Cu to nitrite at $-1.1\ V/_{SCE}$ and to ammonia at $-1.4\ V/_{SCE}$ with high yields. $CuInSe_2$ served as a photocathode producing mixtures of ammonia, nitrite and hydrogen when exposed to light.

Li and co-workers [81] considered Ni, Pb, Zn and Fe cathodes and found that all of them gave an intermediate formation of nitrite with ammonia as the final product. The controlled potential for Pb was $-2.0\ V/_{SCE}$, while for the others it was $-1.5\ V/_{SCE}$. The Zn and Pb cathodes gave over 90% nitrate reduction after an electrolysis time of 60 min.

Lead appears to be the best cathode material in terms of current efficiency for nitrate and nitrite reduction in a synthetic mix that is 1.95 M $NaNO_3$/0.60 M $NaNO_2$/1.33 M NaOH [82]. The divided cell was operated at high current densities (300–600 mA cm^{-2}) and at 80°C. Efficient reduction of the nitrate and nitrite was achieved, resulting in nitrogen, ammonia or nitrous oxide. Nickel performed just about as well as Pb [83] and may have to serve as an alternative [84]. There is always the possibility that through long-term use of a metal cathode slow corrosion might occur, whereby some metal would be lost and possibly contaminate the environment. The Ni cathode would have less tendency to corrode.

One way to avoid metal corrosion is to cover the electrode with an electrocatalyst. This may also have the possibility of shifting the potential to more positive values by lowering the overpotential. Glassy carbon electrodes have been covered with several different, highly stable metal phthalocyanines (MPc) and nitrate reduction carried out with them in basic solution [85]. CuPc was found to be the best in producing high yields of ammonia.

The mechanism for the electrolytic reduction of nitrate is complex; however, Bockris and Kim [86] have proposed a mechanism based on their studies in highly alkaline solution. The steps shown below were developed from the current–voltage curve. Further reduction products of NO were omitted since they did not effect the curve.

$$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^- \quad \text{(equilibrium)}$$

$$NO_2^- + H_2O \rightarrow NO^+ + 2OH^- \quad \text{(rds)}$$

$$NO^+ + e^- = NO \quad \text{(equilibrium)}$$

The commercial application of nitrate reduction by electrochemical techniques is underway. It may lead to the generation of a variety of nitrogen species in a less expensive way than they are presently being obtained [13]. A recent patent [87] describes the generation of ammonia from nitrate by electrolysis to protect carbon steel water pipes from corrosion. The application has also led to patents that demonstrate how nitrate might be removed from raw water electrochemically [88,89].

3.2. Photochemical

Recent studies have focused on using light to activate the nitrate ion directly or to activate a catalyst that then activates the nitrate for reaction with a reducing agent. One example of the first case is the photoinduced formation of oxygen species from nitrate to react with humic materials in water [59]. Complex humic materials are ubiquitous in soils and natural waters. They along with nitrate and nitrite salts in water are able to attack and convert organic compounds. The following reactions occur when nitrate and nitrite salt solutions are photolyzed between 290 and 400 nm in N_2:

$$NO_3^- + H_2O \rightarrow NO_2 + OH^- + {}^{\bullet}OH$$

$$NO_2^- + H_2O \rightarrow NO + OH^- + {}^{\bullet}OH$$

When a pH 9.60 solution of humic materials containing benzene and cumene is photolyzed, oxidizing species, as shown by ESR, are produced (${}^{\bullet}OH$ is noted to be the most aggressive oxidant in the natural environment [90]). Adding nitrate and increasing its concentration causes a significant increase in the concentration of the oxidizing species. When the light is turned off, the oxidizing species disappear.

The photochemically induced reduction of nitrate in seawater has been studied. The nitrate acts as a primary chromophore, which in the presence of organic material produces nitrite [58]. This ion is a possible source of NO and the reactive hydroxyl radical.

Bilski and co-workers [90] have carried out a detailed study of the UV excitation of nitrite anions in anaerobic aqueous solution in the presence of organic and inorganic substrates. The potential of nitrite to photogenerate radical products was demonstrated.

Reducing nitrate with water (as in the following equation) is an ‘up-hill’ energy process with a ΔG value of 269 kJ; however, with the proper photocatalyst it might be driven by light.

$$2HNO_3 + H_2O \rightarrow NH_4NO_3 + 2O_2$$

$$2HNO_3 + H_2O \rightarrow NH_4NO_3 + 2O_2$$

When a 1 M $NaNO_3$/O.1 M NaOH solution is irradiated with a 500 W Xe arc lamp and a Pt–TiO_2 powder impregnated photocatalyst is present, nitrite forms at a rate of 2.8 μmol h^{-1}. However, when a 1 M HNO_3 solution is subjected to the same conditions, 2.4 μmol h^{-1} of ammonia form [91]. O_2 is also formed in both instances.

A photocatalytic reduction of nitrate has been carried out using H_2TiO_4/CdS nanocomposites in which CdS particles of less than 0.8 nm thick are incorporated into the interlayers of $H_2Ti_4O_9$ [92]. When a 1 mM NO_3^- solution with methanol present is exposed to UV light from a 100 W high pressure Hg lamp, within 20 h the nitrate has completely decomposed to nitrite and ammonia. The methanol serves as a sacrificial reductant that prevents the CdS from oxidizing. Kogel and Monbouquette [93] have shown that with quantum-sized CdS nanocrystals electron redox potentials can be tuned to sufficiently negative potential to enable nitrate reduction at neutral pH.

3.3. Thermal

Heating a solid nitrate in an inert atmosphere eventually produces nitrogen oxides and one of the first detailed thermal studies was of the thermal decomposition of $NaNO_3$ by Freeman [94]. An equilibrium constant of 1.41 at 700°C was found for the reaction:

$$NaNO_2(l) + \tfrac{1}{2}O_2(g) \Leftrightarrow NaNO_2(l)$$

The reaction has a ΔH value of -102.6 kJ mol^{-1}. Above 700°C the $NaNO_2$ decomposes to produce nitrogen oxides.

Heating nitrates with a variety of materials in air to high temperatures also leads, in most instances, to the formation of nitrogen oxides. NO_x is produced when nitrate-containing nuclear waste is heated to 400°C with H_3PO_4 in a 2:1 nitrate:phosphate ratio and then, allowed to go to dryness [95]. The thermal decomposition of some heavy metal nitrates has shown that first, the nitrite and oxygen appear, then the oxides of nitrogen form [96]. Lutze [97] states that in Europe, nuclear wastes with high concentrations of nitric acid are heated to 600–900°C to decompose the nitrate.

Since sodium nitrite is an important constituent of a common heat transfer fluid, its thermal decomposition has been studied in considerable detail at 350 and 650°C with NO_x being the primary product. A variety of effects on decomposition, such as, surrounding atmosphere, particle size and surface area have been examined. The most important factor affecting the process is temperature [98].

Several of the reports discussed in the sections above involve high temperature aqueous reactions. The hydrothermal processes examined recently by Cox et al. [36] have had formic acid, glucose, ammonia, and hydrogen reacting in solution with the nitrate at high temperature and pressure. Others [37–39] have studied the reaction of nitrate with ammonia under hydrothermal conditions.

Thermal studies of nitrates with a cation that might serve as a reducing agent, such as NH_4NO_3 and $[NH_3OH]NO_3$, have been studied, but were discussed above in other sections of this report (see Section 3.2).

An unusual high temperature study dealing with nitrate reduction is that of Hutson and Sen [99]. The reaction of nitrate with several organic compounds (methane, ethanol, *n*-propanol, THF, acetic acid and ethane) reacted with nitrate in 96% sulfuric acid at temperatures 170–190°C to produce high yields of the ammonium ion. Even H_2 gas was able to reduce nitrate under these conditions (20% yield). These experiments represented unprecedented examples of the reduction of ionic nitrate in an oxidizing environment.

4. A final comment

Removing nitrate from water by chemical reduction is not a simple, straightforward chemical operation. Unfortunately there is no reducing agent that can be mixed directly with a nitrate solution at room temperature to rapidly produce a lower oxidation state of nitrogen. A catalyst is required or some heat or other energy source needs to be applied. The reactions are kinetically, not thermodynamically controlled.

There is a great effort being made to find ways to destroy nitrate in aqueous solution. The best way to achieve this may be to combine several methods, rather than depend on a single one. For example, a chemical method might be used to obtain nitrite, and then an electrochemical method might be used to achieve N_2 or ammonia. Since borohydride reacts with nitrate to generate ammonia and hydrogen, the addition of a Cu–Pd catalyst to the mixture might allow all of the reducing power of the borohydride to be used for nitrate reduction. The Cu–Pd catalyst served as a good catalyst for the H_2 reduction of nitrate [67]. Photoactivating the nitrate ion in the presence of a suitable reducing agent needs to be examined. The solution of this problem will require some innovative chemical approaches.

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