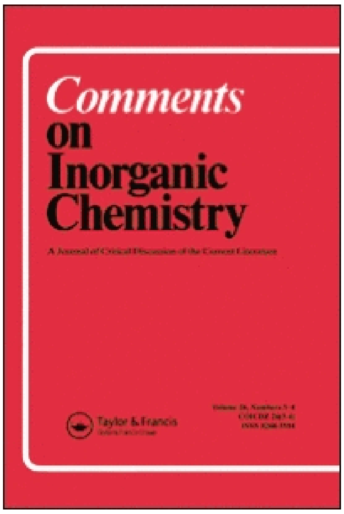

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Kinetics and Mechanism of Autocatalytic Nitric Acid Oxidations

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To cite this Article Bazsa, GyÖrgy and Epstein, Irving R.(1986) 'Kinetics and Mechanism of Autocatalytic Nitric Acid Oxidations', Comments on Inorganic Chemistry, 5: 2, 57 — 87

To link to this Article: DOI: 10.1080/02603598608072276

URL: http://dx.doi.org/10.1080/02603598608072276

Kinetics and Mechanism of Autocatalytic Nitric Acid Oxidations

A wide range of inorganic substrates undergo autocatalytic oxidation by moderately concentrated (1–4 M) nitric acid. In addition to behaving as clock reactions in closed (batch) systems, several of these oxidations exhibit bistability in open continuous-flow stirred tank reactor (CSTR) systems and wave propagation in unstirred configurations. Analysis of experimental studies, combined with detailed numerical simulation, suggests several mechanistic features which are common to nitric acid oxidations. The mechanistic scheme also affords insight into why nitric acid oxidations, in contrast to many other autocatalytic reactions, have defied efforts to convert them into chemical oscillators.

INTRODUCTION

Nitric acid is one of the best known and most widely applied oxidizing agents in chemistry. Moderately concentrated nitric acid is a facile oxidant of many organic and inorganic compounds. While nitric acid may also serve as a nitrating[1] or nitrosating[2] agent, these latter reactions are outside the scope of this Comment.

Many, but not all, nitric acid reactions are autocatalytic in nature. This characteristic kinetic feature is reflected in some common observations:

(1) There is an induction period followed by a stage of rapid product formation (reactant consumption).

(2) Even very low initial concentrations of nitrite or nitrous acid significantly shorten the induction period.

Comments Inorg. Chem.
1986, Vol. 5, No. 2, pp. 57–87
0260-3594/86/0502-0057/$30.00/0

(3) Species such as azide or hydrazine, which scavenge nitrite, increase the length of the induction period or, at higher concentrations, totally inhibit the reaction.

Our interest in nitric acid oxidations arose initially from the fact that autocatalytic reactions have proven to be important both theoretically[3] and experimentally[4] in the design of homogeneous oscillating chemical reactions. We comment briefly below on the lack of success to date of efforts to construct chemical oscillators based on nitrate oxidation reactions.

A survey of the literature[5-7] suggests that the autocatalytic nature of nitric acid oxidations is recognized and the accelerating effect of nitrite is utilized in many preparative methods,[8] but that the number of studies in which kinetic results are presented is extremely limited. In particular, very little attention has been devoted to the kinetics of the induction period.

We summarize briefly the relevant chemistry and then attempt to construct a self-consistent scheme for autocatalytic nitric acid oxidations. In spite of the wide variety of species which undergo these reactions, important chemical features are to be found in common, much as is the case for autocatalytic bromate oxidations.[9]

POSITIVE OXIDATION STATES OF NITROGEN

Nitrogen probably exists in more stable oxidation states than any other element, possessing at least nine oxidation states ranging from -3 to $+5$. It is clear from the extensive literature that N(V) in the form of nitric acid may be reduced to a number of different final oxidation states depending upon the reductant and even more importantly upon the initial concentration of nitric acid. It is not unusual for nitric acid oxidations to be nonstoichiometric and for products and product ratios to vary in an ill-defined fashion with initial concentrations. Oxidations of negative oxidation states of nitrogen by nitric acid are often particularly complex. In spite of these variations and complexities, it seems to be generally true that the N(V) of nitric acid is never reduced to a negative oxidation state in a homogeneous reaction. We therefore confine this Comment to the positive states only.

Nitrogen(V)

Nitric acid is one of the strongest mineral acids known, and is essentially fully dissociated under the conditions of the oxidations to be discussed. No significant amounts of the anhydride N_2O_5 occur at these concentrations, so it is sufficient to consider only H^+ and NO_3^- ions.

Nitrogen(IV)

As in the gas phase, N(IV) occurs in aqueous solution as a monomer–dimer equilibrium mixture of NO_2 and N_2O_4. Grätzel *et al.*[10] give the rate and equilibrium constants of the reaction

$$2NO_2(aq) = N_2O_4(aq) \tag{1}$$

as $k_1 = 4.5 \times 10^8\ M^{-1}\ s^{-1}$ and $K_1 = 7.1 \times 10^4\ M^{-1}$. The latter is in good agreement with the value obtained by Treinin and Hayon[11] in another pulse radiolysis experiment. A number of studies[10–12] make it clear that equilibrium in reaction (1) is established extremely rapidly, so that the question of whether N(IV) reacts as N_2O_4 or as $2NO_2$ has no kinetic significance. As we shall see later, NO_2 concentrations remain well below the solubility limit. A thorough discussion of the kinetics and equilibrium behaviour of the aqueous dissolution of nitrogen oxides has been given by Schwartz and White.[12] The self-ionization of N_2O_4 to NO^+ and NO_3^- is negligible under the conditions of interest.

Nitrogen(III)

The most common compound of N(III) is nitrous acid or its salts, the nitrites. The following equilibria are of significance in aqueous solutions:

$$HNO_2 = H^+ + NO_2^- \qquad K_2 = 5.1 \times 10^{-4}\ M\ ^{13} \tag{2}$$

$$HNO_2 + H^+ = NO^+ + H_2O \qquad K_3 = 5 \times 10^{-7}\ M^{-1}\ ^{5} \tag{3}$$

$$2HNO_2 = N_2O_3 + H_2O \qquad k_4 = 4\ M^{-1}\ s^{-1}$$

$$K_4 = 5.3 \times 10^2\ M^{-1}\ ^{7} \tag{4}$$

Further detailed studies of particular systems are required to clarify the kinetic roles of the individual N(III) species.[14]

Nitrogen(II)

Owing to its unpaired electron, NO is a relatively reactive species. While its hydration is of no kinetic significance, its limited solubility (1.9×10^{-3} M at 25 °C [15]) should be taken into account in reactions in which it is a major product.

Nitrogen(I)

The most common form of N(I), N_2O, is kinetically rather inert. Once formed, it almost always remains as a final product.

Nitrogen(0)

Without doubt, elemental nitrogen N_2 is the most inactive state of nitrogen. It may appear as a product if negative oxidation states of nitrogen are oxidized by HNO_3, but it is never found when N(V) is reduced by species which do not contain nitrogen.

REDOX REACTIONS BETWEEN DIFFERENT OXIDATION STATES OF NITROGEN

Before considering specific nitric acid–substrate interactions, one must first take into account the possible reactions between different oxidation states of nitrogen. These reactions can and do occur in all nitric acid oxidations independent of the nature of the substrate. They play a key role in the early stage of the oxidation owing to the unavoidable presence of small amounts of lower nitrogen oxidation states in all samples of nitric acid.

Much of the fundamental work on these reactions was carried out over half a century ago by Abel and co-workers. Abel and Schmid[16] studied the autocatalytic reaction between nitric oxide and nitric acid:

$$HNO_3 + 2NO + H_2O = 3HNO_2 \tag{5}$$

They proposed the following reaction scheme:

$$H^+ + NO_3^- + HNO_2 = N_2O_4 + H_2O \tag{6}$$

$$N_2O_4 + 2NO + 2H_2O = 4HNO_2 \qquad (7)$$

with reaction (6) being rate determining, in order to account for the observed autocatalysis. This explanation has been supported by later investigators[17,18] working under a variety of conditions. All of these processes are reversible. The reverse reactions in (6) and (7) are equivalent to the disproportionation of N(IV) and N(III), respectively.

Epstein and co-workers[19-21] have employed the following rate laws for reactions (6) and (7) in their computer simulations of nitric acid oxidations:

$$\nu_6 = 1.5 \times 10^{-2}\ \mathrm{M}^{-2}\,\mathrm{s}^{-1}\ [HNO_2][NO_3^-][H^+]$$

$$\nu_{-6} = 1 \times 10^{8}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}\ [NO_2]^2$$

$$\nu_7 = 5.8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}\ [HNO_2]^2$$

$$\nu_{-7} = 2 \times 10^{7}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}\ [NO][NO_2]$$

The rate constants are based on earlier experimental studies[16,22] and are supported by calculations on the kinetics of the Fe^{2+}–HNO_3 reaction.[19,20] If concentrations become suffiently high, then the solubilities of NO and NO_2 must also be taken into account.

If the overall reaction (5) does indeed occur via reactions (6) and (7), then the direct reaction of N(V) with N(II) must be relatively slow, since if it were the major reaction path, the reaction would not be autocatalytic. No direct measurements have been made of the kinetics of reaction (8):

$$NO + NO_3^- + H^+ = NO_2 + HNO_2 \qquad (8)$$

Orban and Epstein[20] give its rate law as

$$\frac{d[NO_2]}{dt} = 5.0 \times 10^{-3}\ \mathrm{M}^{-3}\,\mathrm{s}^{-1}\ [NO_3^-][NO][H^+]^2 - 9.3\ \mathrm{M}^{-2}\,\mathrm{s}^{-1}\ [HNO_2][NO_2][H^+] \qquad (9)$$

where the values of the rate constants and the form of the $[H^+]$ dependence are derived from fitting the calculated and observed Fe^{2+}–HNO_3 kinetics. While increasing k_8 beyond the value given in Eq. (9) significantly affects the calculated region of bistability in simulated CSTR experiments, deleting reaction (8) completely has no qualitative effect on the calculated phase diagram.

AUTOCATALYTIC NITRIC ACID OXIDATIONS

In this section we summarize briefly the known autocatalytic oxidations of inorganic species by nitric acid. We shall not discuss the wide variety of organic substrates which may also be oxidized in an autocatalytic fashion.[8]

Arsenite

Abel and Schmid[23] found that arsenite is oxidized by nitric acid according to the stoichiometry

$$3H_3AsO_3 + 2HNO_3 = 3H_3AsO_4 + 2NO + H_2O \qquad (10)$$

with rate law

$$v_{10} = k_{10}[H_3AsO_3][HNO_2]^2 \qquad (11)$$

They postulate the following mechanism:

$$H^+ + NO_3^- + HNO_2 = N_2O_4 + H_2O \qquad (6')$$

$$N_2O_4 + 2NO + 2H_2O = 4HNO_2 \qquad (7')$$

$$2HNO_2 = N_2O_3 + H_2O \qquad (12)$$

$$N_2O_3 + H_3AsO_3 = H_3AsO_4 + 2NO \qquad (13)$$

where reaction (12) is in rapid equilibrium and reaction (13) is rate determining. While the proposed mechanism does account for the autocatalysis, it is difficult to see why the final product is NO, which should be oxidized by excess HNO_3 via reaction (5).

Thiocyanate

Stedman and co-workers[24,25] investigated the HNO_3–SCN^- reaction under a variety of conditions. They found a transient red intermediate which they identified as NOSCN. The rate laws obtained were

$$\nu_{14} = k_{14}[H^+][NO_3^-][HNO_2] \tag{14}$$

at high $[SCN^-]$, and

$$\nu_{15} = k_{15}[H^+]^2[NO_3^-][HNO_2][SCN^-] \tag{15}$$

at low $[SCN^-]$. The 10-step mechanism they propose involves the formation of N_2O_4 which oxidizes HNCS to hypothiocyanous acid, HOSCN. This latter species is then converted to thiocyanogen. The end products, including H_2SO_4 and HCN, result from the hydrolysis of $(SCN)_2$. No detailed calculations were performed to support the suggested mechanism.

Bazsa and Epstein[21] later studied this reaction both under batch conditions and in continuous-flow stirred reactors (CSTR). The batch results are similar to those obtained by Stedman *et al.* In the CSTR, the system shows bistability and hysteresis, which will be discussed below. A four-step scheme involving only overall reactions for which there is kinetic evidence was proposed:

$$H^+ + NO_3^- + HNO_2 = 2NO_2 + 2H_2O \tag{6'}$$

$$2NO_2 + SCN^- + 3H^+ + 2NO_3^- + 2H_2O = H_2SO_4 + HCN + 4HNO_2 \tag{16}$$

$$HNO_2 + SCN^- + 2H^+ = NOSCNH^+ + H_2O \tag{17}$$

$$2NO_2 + NOSCNH^+ + H^+ + 2NO_3^- + 3H_2O = H_2SO_4 + HCN + 5HNO_2 \tag{18}$$

No attempt was made to decompose the complex reactions (16) and (18) into elementary steps.

The rate laws for Eqs. (6′), (16)–(18) were integrated numerically to predict both the kinetics of individual experiments and the dependence of the reaction on initial concentrations. As can be seen in Fig. 1 and Table I, the calculations are in excellent agreement with experiment. The analysis indicates that NOSCN or, more precisely, its protonated form $NOSCNH^+$ has an essential kinetic role. It provides a more rapid pathway for oxidation (via reaction (18)) than the direct oxidation (reaction (16)) of SCN^- itself.

Ferrous Ion

The reaction of Fe(II) with HNO_3 has been employed as an analytical tool for well over a century.[26] The formation of the colored

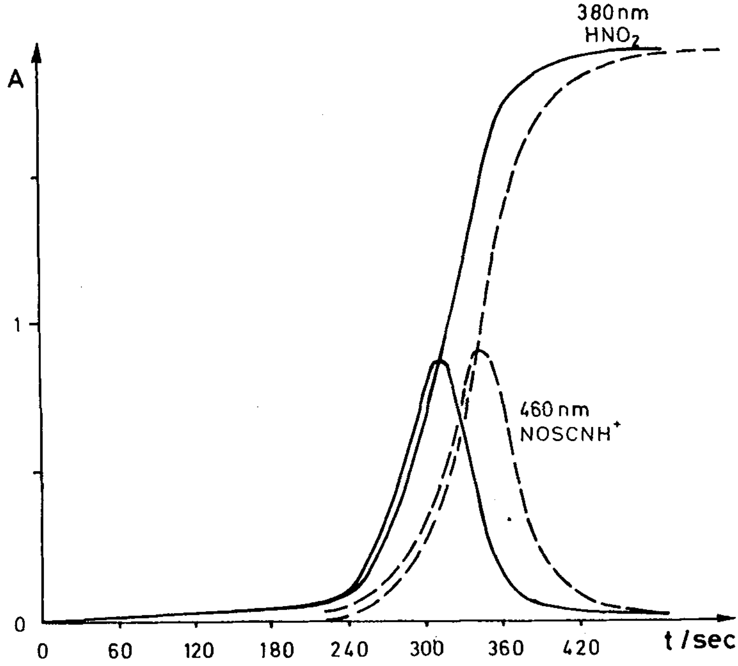

FIGURE 1 Experimental (solid) and calculated (dashed) absorbance curves for the thiocyanate–nitric acid reaction at 25 °C with initial concentrations $[HNO_3]$ = 4 M, $[SCN^-]$ = 0.02 M (Ref. 21).

TABLE I

Experimental and calculated induction times and maximum [$NOSCNH^+$] in the HNO_3–SCN^- reaction (Ref. 21)

		t_i (s)		10^3 [$NOSCNH^+$] (M)	
[HNO_3]$_0$ (M)	[SCN^-]$_0$ (M)	Exp.	Calc.	Exp.	Calc.
2	10	1080	800	2.2	2.31
4	10	402	370	4.1	3.9
6	10	282	260	4.7	4.3
8	10	190	203	4.3	4.77
3	1	1900	2030	0.1	0.1
3	5	702	605	1.20	1.36
3	10	492	490	3.1	3.6
4	1	1050	1400	0.17	0.12
4	5	570	480	1.75	1.54
4	20	340	340	9.0	9.1
5	2	610	610	0.67	0.45
5	5	534	390	2.12	1.67
5	20	456	280	9.72	9.80

$FeNO^{2+}$ complex provides the basis for the well-known brown-ring test[27] employed in the qualitative analysis of nitrites and nitrates. The reaction is a clock reaction, which is apparently autocatalytic.[28]

The first quantitative kinetics study on this reaction appeared in 1980.[19] A seven-step mechanism was constructed and found to give good agreement with the observed batch kinetics. The mechanism consists of the oxidation of Fe(II) by N(V), N(IV) and N(III), the rapid equilibrium formation and decomposition of $FeNO^{2+}$, reactions (6) and (8) plus a third reaction involving nitrogen species of different oxidation states, the disproportionation of nitrous acid:

$$2HNO_2 = NO + NO_2 + H_2O \qquad (7')$$

It is notable that the $FeNO^{2+}$ intermediate is kinetically inactive. The reaction was studied under flow conditions[20] and good agreement was again obtained between the predictions of the mechanism and experiment. The CSTR behavior is discussed below.

Studies of the reactions of iron(II) complexes with nitric acid have revealed some interesting results. The tris(1,10-phenanthroline) complex, ferroin, exhibits autocatalytic behavior with a dramatic red–blue color change.[29] However, the tris(3,4,7,8-tetramethyl-1,10-phenanthroline) complex, Fe^{II} TMP does not show autocatalytic behavior, even though it has a redox potential within 0.04 V of the hexa-aquo species.[30] Numerical simulations of the Fe^{II} TMP–nitrous acid reaction suggest that the lack of autocatalysis results from the preferential reaction in the TMP complex of NO with the ferric rather than with the ferrous species as in the hexa-aquo complex.[30]

Hydroxylamine

The nitric acid oxidation of NH_2OH has been studied by Stedman and co-workers[31,32] and by Bennett *et al.*[33] The course of the reaction changes markedly with the nitric acid concentration and with the $[HNO_3]_0/[NH_2OH]_0$ ratio. At low acid concentrations, N_2O is the major product:

$$NH_2OH + HNO_2 = N_2O + 2H_2O \tag{19}$$

At a sufficiently high level of $[HNO_3]$, about 2.5 M depending upon $[NH_2OH]$, hydroxylamine switches its role from scavenger to producer of nitrous acid, and the reaction becomes autocatalytic with stoichiometry

$$NH_2OH + 2HNO_3 \rightarrow 3HNO_2 + H_2O \tag{20}$$

Gowland and Stedman[32] give a "phase diagram" showing the temperature and initial concentrations for which the dominant reaction is (19) or (20). Bennett *et al.*[33] point out that when the initial hydroxylamine concentration is low, still another product, N_2, is found.

The mechanism proposed[32] consists of the following reactions:

$$H^+ + NO_3^- + HNO_2 = N_2O_4 + H_2O \tag{6}$$

$$NH_2OH + N_2O_4 \rightarrow HNO + N_2O_3 + H_2O \tag{21}$$

$$HNO + N_2O_4 \rightarrow HNO_2 + N_2O_3 \tag{22}$$

$$N_2O_3 + H_2O = 2HNO_2 \tag{-12}$$

$$HNO_2 + NH_3OH^+ \rightarrow N_2O + H_2O + H_3O^+ \qquad (23)$$

Formation of HNO_2 rather than N_2O is favored by a high $[HNO_3]_0/[NH_2OH]_0$ ratio, allowing HNO_2 to react by the autocatalytic pathway 2 × (6) + (21) + (22) − (12) rather than by the nitrosation of NH_3OH^+, reaction (23). Simplified rate laws are derived by a steady state treatment, and numerical calculations give qualitative agreement with experiment.[32] Bennett *et al.* augment the above mechanism with the reaction between HNO_2 and hyponitrous acid to account for the N_2 observed at low $[NH_2OH]$:

$$HNO_2 + NH_3OH^+ \rightarrow H_2N_2O_2 + H_2O + H^+ \qquad (24)$$

$$HNO_2 + H_2N_2O_2 \rightarrow HNO_3 + N_2 + H_2O \qquad (25)$$

Also,

$$H_2N_2O_2 \rightarrow N_2O + H_2O \qquad (26)$$

While the combined mechanism appears qualitatively satisfactory, more detailed studies are needed for fix the quantitative values of the various rate constants.

Bromide

Two studies of the oxidation of bromide by nitric acid[34,35] find a rate law that is first order in bromide ion and 3/2 order in $[HNO_2]$, with $[NO_3^-]$ exerting a remarkably small effect. The stoichiometry is

$$2HBr + HNO_3 = Br_2 + HNO_2 + H_2O \qquad (27)$$

The rate also depends strongly upon the acidity and the ionic strength.

Longstaff[34] proposes a mechanism in which the key intermediate is N_2O_3Br (or $N_2O_3BrH^+$) to account for the unusual nitrous acid dependence. No detailed calculations have been carried out.

Sulfite

Sulfite ion is oxidized by nitric acid only in the presence of added HNO_2. In a narrow concentration range of HNO_3, the reaction is autocatalytic with an induction period that can be shortened or eliminated by the addition of nitrous acid.[36] Vesprek-Siska and Uher[36] propose a general kinetic scheme for the reaction, but draw no quantitative conclusions. Our own experiments confirm the autocatalytic behavior, but exhibit some lack of reproducibility, apparently owing to a considerable sensitivity to the rate and manner of stirring, a phenomenon seen in several other autocatalytic, bistable reactions in recent CSTR experiments.[37,38]

Vanadium(IV)

Kummer[39] reports that the oxidation of vanadyl ion, VO^{2+}, by nitrate in acidic solution at 80 °C shows an induction period of some 10 min followed by rapid evolution of NO gas. He points out the autocatalytic nature of the process but offers no mechanistic explanation.

Formaldehyde and Formic Acid

The reaction of nitric acid with HCHO and HCOOH has been employed in the removal of nitric acid from mixtures. Healy[40] found an induction period that was shortened by addition of $NaNO_2$, N_2O_5 or NO_2. While the nitric acid oxidation was not the major focus of this work, it clearly demonstrates the autocatalytic nature of these reactions.

CSTR EXPERIMENTS

In the past five years the study of autocatalytic reactions in flow reactors has provided a great deal of information both about the variety of possible dynamical behavior[41] and about mechanisms of individual systems.[42] Among the most interesting phenomena which can occur in a system of this type are chemical oscillation[43] and bistability,[41] the existence of two different stable steady states under the same set of external conditions (temperature, pressure, input concentrations, flow rate). Bistability is associated with the existence of hysteresis and a "memory effect," since the final state of the system will depend upon the past history of that system. We have studied several nitrate oxidations in the CSTR, and we summarize our results here.

Fe^{2+}–HNO_3

The ferrous–nitric acid reaction in a CSTR has been investigated by Orbán and Epstein,[20] who also carried out extensive numerical simulations using the mechanism developed[19] for the batch reaction. A wide region of bistability is obtained both in the experiments and in the calculations. As Fig. 2 shows, the agreement is quite good, particularly for the transition from the low potential (flow) steady state SSI to the high potential (thermodynamic) state SSII. Table II gives the calculated concentrations for the two steady states which are stable under the same set of external conditions. The deviations of the major species concentrations in SSII from the composition of the input flow are consistent with the overall reaction stoichiometry.

$$2Fe^{2+} + NO_3^- + 3H^+ = 2Fe^{3+} + HNO_2 + H_2O \qquad (28)$$

Transitions between the two steady states were induced experimentally by sufficiently large injections of NO_2^- (SSI → SSII) or SO_3^{2-} (SSII → SSI). These perturbation experiments, illustrated in Fig. 3, were also simulated successfully on the computer.

SCN^-–HNO_3

The thiocyanate–nitric acid reaction has been studied[21] in the CSTR and the region of bistability mapped out as the flow rate and input $[SCN^-]$ and $[HNO_3]$ are varied. The flow reaction has been simulated using the mechanism developed for the batch reaction, Eqs. (6′), (16)–(18). Again, as shown in Fig. 4, the agreement between theory and experiment is quite good.

SO_3^{2-}–HNO_3

Preliminary studies of the sulfite–nitric acid reaction reveal a broad range of bistability extending beyond the experimentally accessible

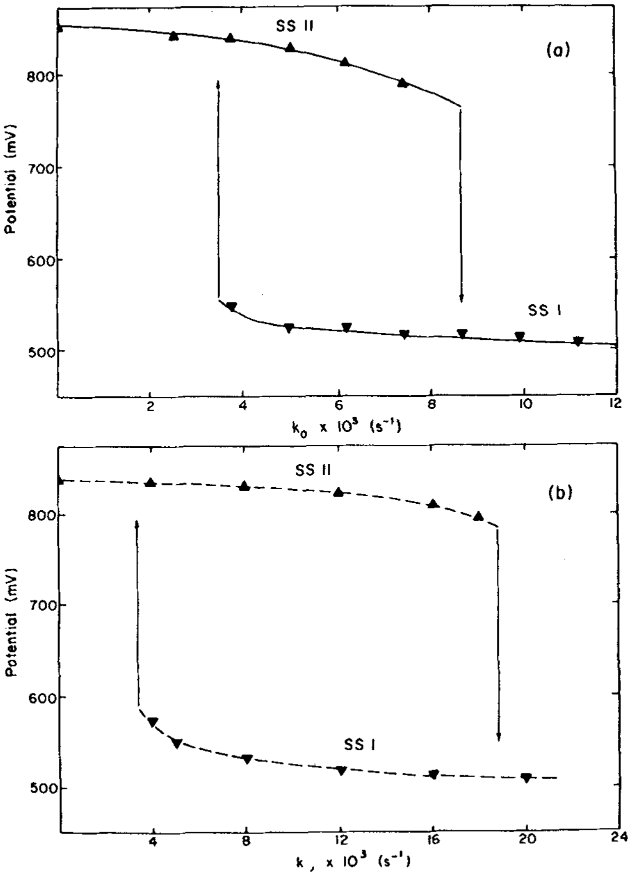

FIGURE 2 Steady state potential of a platinum redox electrode (V) and absorbance at 450 nm (A) as functions of flow rate k_0 in a CSTR with [Fe^{2+}] = 0.075 M, [HNO_3]$_0$ = 1.25 M: (a) observed V vs. k_0, (b) calculated V vs. k_0, (c) observed A vs. k_0, (d) calculated A vs. k_0. Vertical arrows indicate transitions between different branches of states: (SSI) high [Fe^{2+}], low [$Fe(NO)^{2+}$] (low potential state); (SSII) low [Fe^{2+}], high [$Fe(NO)^{2+}$] (high potential state) (Ref. 20).

upper limit of flow rates. Transitions between the bistable states can be induced by addition of oxidizing or reducing species. Both states are excitable in the sense that small perturbations (e.g., injection of azide or nitrite) can induce large excursions from the

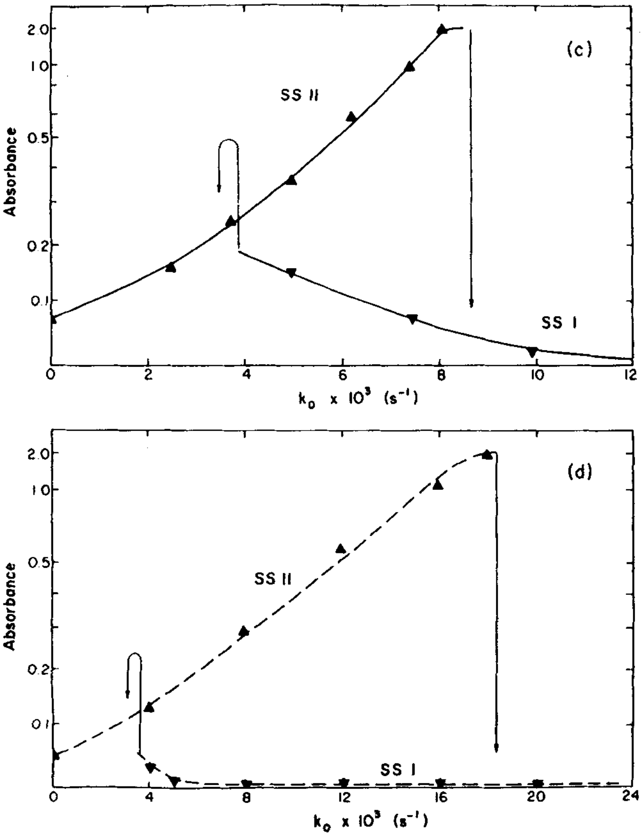

FIGURE 2 (continued)

initial concentrations before the system relaxes back to the steady state.

NH_2OH–HNO_3

No evidence of bistability was found in the hydroxylamine–nitric acid reaction in the following range of conditions: 4 M $\leq [HNO_3]_0 \leq$ 5 M, 1×10^{-3} M $\leq [NH_2OH]_0 \leq 3 \times 10^{-3}$ M, $2 \times 10^{-1}\ s^{-1} < k_0 < 3.6 \times 10^2\ s^{-1}$, where the subscript zero represents input concentration corrected for dilution (mixing) and k_0 is the reciprocal residence time (flow rate) in the reactor.

TABLE II

Calculated steady state concentrations (M) with $[Fe^{2+}]_0 = 0.075$ M $[HNO_3]_0 = 1.50$ M, $k_0 = 8 \times 10^{-3}\ s^{-1}$

	$[Fe^{2+}]$	$[Fe^{3+}]$	$[FeNO^{2+}]$	$[NO_3^-]$	$[NO_2]$	$[HNO_2]$	$[NO]$	$[H^+]$
Low Pot. State	7.5×10^{-2}	2.3×10^{-4}	4.9×10^{-5}	1.50	4.2×10^{-10}	1.4×10^{-5}	1.5×10^{-6}	1.50
High Pot. State	3.3×10^{-3}	7.2×10^{-2}	2.0×10^{-4}	1.46	3.1×10^{-6}	3.6×10^{-2}	1.3×10^{-4}	1.39
Δ[a]	−0.0717	0.0717		−0.037		0.036		−0.110
$\Delta/(0.036)$	−1.99	1.99		−1.03		1.00		−3.06

[a] Change from input flow, i.e., net production or consumption of major species in the reactor.

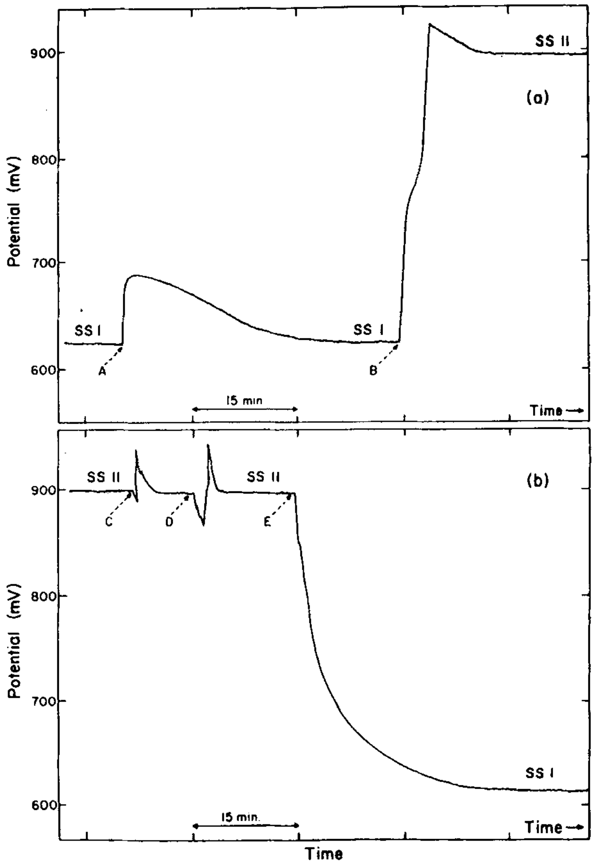

FIGURE 3 Perturbation experiments with $[Fe^{2+}]_0 = 0.125$ M, $[HNO_3]_0 = 1.25$ M, $k_0 = 4.9 \times 10^{-3}\ s^{-1}$: (a) transition from SSI to SSII by nitrite perturbation; (b) transition from SSII to SSI by sulfite perturbation. At the lettered points the following concentration perturbations were made by a single rapid addition of the appropriate reagent: (A) $\Delta[NO_2^-] = 1.8 \times 10^{-2}$ M, (B) $\Delta[NO_2] = 7.2 \times 10^{-2}$ M, (C) $\Delta[SO_3^{2-}] = 1.0 \times 10^{-2}$ M, (D) $\Delta[SO_3^{2-}] = 2.5 \times 10^{-2}$ M, (E) $\Delta[SO_3^{2-}] = 3.6 \times 10^{-2}$ M (Ref. 20).

TRAVELING WAVES

One of the most remarkable and potentially significant phenomena associated with autocatalytic reactions is the ability of certain of

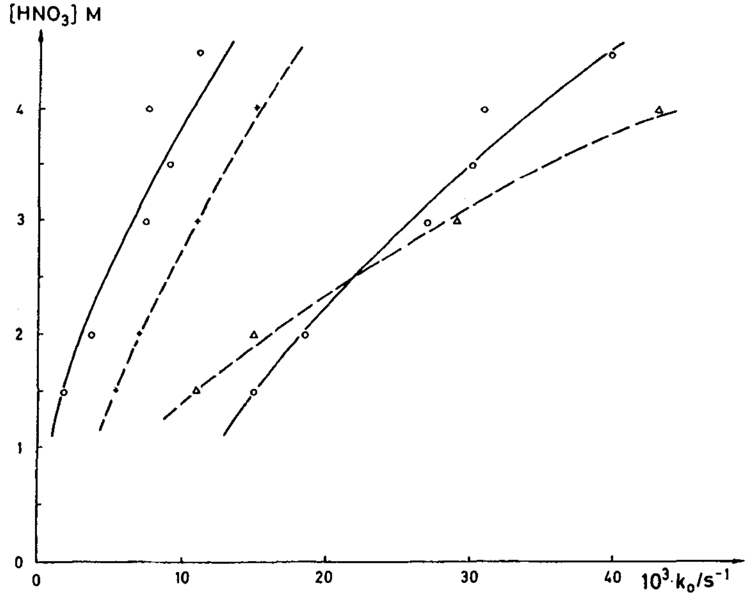

FIGURE 4 Phase diagram for the SCN^-–HNO_3 reaction in the flow rate (k_0)–$[HNO_3]_0$ plane with $[SCN^-]_0 = 0.01$ M. Pairs of lines bound the region of bistability. Solid lines and ○, experimental data. Dashed lines and +, △, calculated (Ref. 21).

these systems to develop and propagate spatially inhomogeneous concentration patterns in an initially homogenous, unstirred solution. While spatial pattern formation and wave propagation have been most thoroughly studied in the Belousov–Zhabotinskii reaction,[44] novel wave phenomena have been observed in two nitrate oxidation reactions, and we describe them below.

Fe(II)–HNO_3

If the ferrous–nitric acid reaction is carried out in an unstirred beaker or test tube, the change from colorless to brown occurs nonuniformly, but so rapidly that it is exceedingly difficult to characterize any inhomogeneities present. If the HNO_2 present in the nitric acid is first scavenged by the addition of a small amount ($\sim 10^{-4}$ M) of hydrazine or azide, the Fe(II)–HNO_3 mixture is stable for hours rather than minutes, and when the color change does begin, a brown wave front moves through the solution with a velocity of mm/min. The wave is most conveniently observed by initiating it, either in a test tube or a petri dish, by touching the solution with a wire that has been dipped in a concentrated nitrite solution.

Bazsa and Epstein[45] have studied these waves in both one-dimensional (test tube) and two-dimensional (petri dish) geometries. They have measured wave velocities as functions of the initial ferrous ion and nitric acid concentrations. (The scavenger concentration affects only the induction period and not the wave velocity.) Although the waves move significantly more rapidly than in other autocatalytic reactions,[44,46-48] the results obtained are qualitatively similar.

The Fe^{2+}–HNO_3 waves do exhibit one surprising new phenomenon, however. The wave velocity in a tube is approximately six

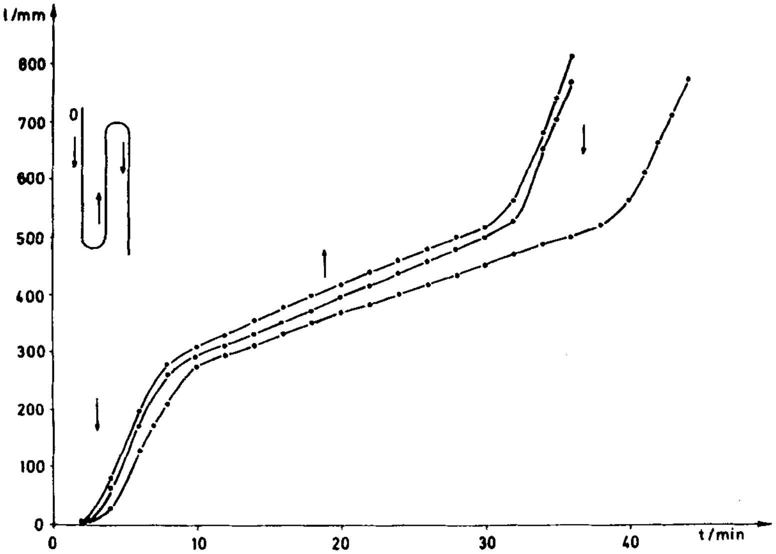

FIGURE 5 Wave propagation in the Fe^{2+}–HNO_3–HNO_3 reaction. Graph shows three replicate determinations of distance (l) from point of initiation as a function of time (t) after mixing reagents in a glass tube of 2.5 mm i.d. Initial concentrations: $[HNO_3] = 3$ M, $[Fe(II)] = 0.2$ M, $[N_2H_4] = 1 \times 10^{-4}$ M. Arrows indicate direction of wave propagation. Drawing at upper left shows shape of tube.

times greater when the waves move down the tube than when they are moving upward! This astonishing behavior is shown in Fig. 5. Bazsa and Epstein[45] attribute this "gravity effect" to convective mixing induced by the exothermicity of the reaction. This explanation is supported by experiments conducted in a gel which increases the solvent viscosity and causes the upward and downward traveling waves to move at the same (lower) velocity.

NH_2OH–HNO_3

Gowland and Stedman[49] have studied the hydroxylamine–nitric acid reaction under conditions where the system undergoes a transition from the stoichiometry of reaction (19), i.e., scavenging of HNO_2 by hydroxylamine, to reaction (20), autocatalytic production of HNO_2. Under these conditions, an initially homogeneous solution approximately 0.1 M in NH_2OH and 4 M in HNO_3 can spontaneously form two layers, both of which are colorless but differ in their index refraction. The upper layer contains nitrous acid, but no hydroxylamine, while the lower layer shows no HNO_2 absorption, but has a hydroxylamine concentration equal to that of the starting mixture.

The boundary between the two layers moves steadily downward until all the hydroxylamine is consumed. The authors suggest that the significant exothermicity (a 4 °C temperature rise is typical) and surface tension (the phenomenon occurs in silica cells, but not in glass test tubes) are major factors in generating and supporting the boundary.

REMARKS ON THE KINETIC ANALYSIS OF AUTOCATALYTIC REACTIONS

In traditional chemical kinetics studies, one performs experiments to establish the rate equation of the reaction, which usually means determining the order with respect to each of the reactants. The rate equation is then integrated and the rate constant(s) calculated by a least squares fit of the experimental data to the integrated rate law. In some cases, initial rate data will suffice. In more complex systems, various simplifications, such as steady state or pre-equilibrium approximations, may be utilized to overcome the problem of obtaining exact integrated rate laws. Improvements in high-speed electronic computers have made it possible to integrate numerically even very large systems of coupled differential equations. Special programs have been developed to deal with the problem of stiffness, i.e., the existence of multiple timescales in the solutions to the equations.[50]

Except in the case of simple model systems,[51] numerical integration is a necessary tool for kineticists wishing to analyze autocatalytic reactions. Only through the use of numerical techniques is it possible to compare in detail experimental data with mechanistic interpretations and to predict kinetic curves under any desired starting conditions.

It is only quite recently that detailed computer simulations have been carried out on autocatalytic nitric acid reactions.[19-21] Many previous workers utilized relatively high initial concentrations of nitrite to eliminate the induction period, a particularly difficult problem to deal with by traditional methods. Evaluation of the typical S-shaped curve associated with an autocatalytic reaction is not a trivial task. One must first choose a quantity for measurement. Often, classical analytical procedures may be applied. Spectrophotometric measurements, if feasible, are often the method of choice, since continuous monitoring of a single species can be performed. In nitric acid systems one can follow either HNO_2, an intermediate such as $FeNO^{2+}$ or $NOSCNH^+$, or a product such as Br_2. In nonstoichiometric reactions, more than one species should be monitored.

Figure 6 shows a typical kinetic curve for an autocatalytic reaction. Characteristics which may serve as the basis for a quantitative evaluation are indicated. These are: (a) the length of the induction period, which may be taken either as t_i or as $t_{1/2}$; (b) the rate of the reaction $r_{1/2}$ at $t_{1/2}$, which is essentially the maximum rate; and (c) the final product concentration A_∞. Experimental studies should be designed to reveal the influence of initial concentrations (and possibly temperature) on each of these quantities. One should not in general expect to be able to derive a single "classical" rate equation, since if any intermediate ever builds up to a measurable concentration, as is likely in an autocatalytic reaction, then the system cannot be described by just one kinetic equation.

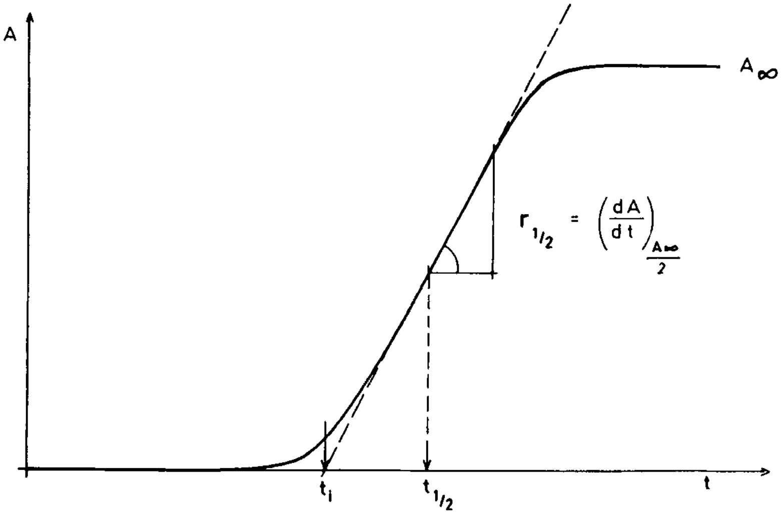

FIGURE 6 Characteristic parameters for analyzing kinetic curves of autocatalytic reactions.

Once a mechanism has been postulated, one can calculate kinetic curves under the appropriate experimental conditions. Rate constants may be varied in a chemically plausible range to get the best fit of the available data. More sophisticated methods[52] are available to assess the sensitivity of the calculated results to changes in initial concentrations or rate constants. Often, the elementary steps included in the mechanism will be modified as a result of the comparison until a satisfactory set of reactions is arrived at.

GENERAL MECHANISTIC CONSIDERATIONS FOR NITRIC ACID OXIDATIONS

Most of the mechanisms proposed in the investigations cited above involve reaction (6) in their explanation of autocatalysis:

$$H^+ + NO_3^- + HNO_2 = N_2O_4 + H_2O \qquad (6)$$

However, as our computer studies have shown, there exists a common misinterpretation of the kinetic role of reaction (6). In many of these schemes, the reaction is taken to be a rapid pre-equilibrium, shifted somewhat to the left. In some cases a steady state approximation is applied to N_2O_4. Our calculations show that these approximations are not justified.

We carried out a number of model calculations on reaction (5):

$$HNO_3 + 2NO + H_2O = 3HNO_2 \tag{5}$$

using the following rate equations:

$$v_6 = k_6 [H^+][NO_3^-][HNO_2] - k_{-6}[NO_2]^2$$

$$v_7 = k_7 [HNO_2]^2 - k_{-7} [NO][NO_2]$$

In one set of calculations, the value of k_{-7} was fixed at the experimentally determined 2×10^7 M^{-1} s^{-1}, and k_6 was varied. The reverse rate constant k_{-6} was changed to maintain the thermodynamically established ratio $K_6 = k_6/k_{-6} = 1.5 \times 10^{-10} M^{-1}$. In Table III we summarize the effects of varying k_6 on the kinetic features of the reaction. From the sizeable variation of the induction time and the maximum rate, we conclude that step (6) is not in fact a rapid pre-equilibrium.

A second set of calculations, also shown in Table III, was carried out to assess the effects of changes in k_{-7} (and k_7, keeping the ratio fixed). With k_6 fixed at 0.015 M^{-2} s^{-1}, the value of k_{-7} has a negligible effect on the kinetics when k_{-7} is between 10^6 M^{-1} s^{-1} and 10^9 M^{-1} s^{-1}. If k_{-7} is given a lower value ($\sim 10^4$ M^{-1} s^{-1}), the predicted kinetics are changed and become less sensitive to variations in k_6.

It is clear from these calculations that there is no single "rate-determining" step in a mechanism of this type. Several (if not all) steps influence the kinetic course of the reaction. Similar results are obtained in calculations on the HNO_3 + Fe(II) and HNO_3 + SCN^- systems.[20,21] It is significant in the latter two calculations that the same rate equations and rate constants were utilized for reaction (6) and that these are consistent with Abel's data.[16] It seems clear that reaction (6), though always *one* of the rate-determining steps, can never be taken to be a pre-equilibrium in

TABLE III

Influence of rate constants for the HNO_3 + NO reaction on the calculated kinetic features of the reaction. $k_6/k_{-6} = 1.5 \times 10^{-10}$, $k_7/k_{-7} = 3.45 \times 10^{-6}$, $[HNO_3]_0 = 4$ M, $[NO]_0 = 0.01$ M in all cases

k_6 ($M^{-2}s^{-1}$)	k_{-7} ($M^{-2}s^{-1}$)	$[HNO_2]_0$ (M)	t_i (s)	$1/t_i$ (s^{-1})	$r_{1/2}$ ($M\ s^{-1}$)
0.005	2×10^7	1×10^{-7}	46.7	0.021	1.78
0.010	"	"	23.4	0.042	3.67
0.015	"	"	15.6	0.064	5.39
0.030	"	"	7.8	0.128	10.80
0.045	"	"	5.2	0.192	16.16
0.075	"	"	3.12	0.320	26.70
0.005	2×10^4	1×10^{-7}	55.0	0.018	0.53
0.010	"	"	33.6	0.030	0.58
0.015	"	"	26.83	0.037	0.598
0.030	"	"	20.0	0.050	0.66
0.075	"	"	16.7	0.060	0.67
0.015	2×10^4	1×10^{-7}	26.83	0.037	0.598
"	4×10^4	"	20.32	0.049	1.12
"	8×10^4	"	17.40	0.057	1.98
"	2×10^5	"	16.0	0.0625	3.60
"	2×10^6	"	15.6	0.064	5.35
"	2×10^7	"	15.6	0.064	5.39
0.015	2×10^7	1×10^{-8}	18.8	0.053	5.40
"	"	1×10^{-7}	15.6	0.064	5.40
"	"	1×10^{-6}	12.4	0.081	5.4
"	"	1×10^{-5}	9.2	0.109	5.4
"	"	1×10^{-4}	6.0	0.167	5.4
"	"	1×10^{-3}	2.8	0.357	5.7

autocatalytic nitric acid oxidations, at least until the reaction is quite near completion.

In order for a mechanism to produce the observed autocatalysis it must account for the reduction of N(IV), either as NO_2 or N_2O_4. Autocatalysis occurs because from the one N(III) consumed in reaction (6), two HNO_2 ultimately evolve from the two N(IV) produced. From this observation we deduce a second general feature of these autocatalytic oxidations: the redox reaction between substrate and N(IV), rather than the direct reduction of N(V), must be the major pathway. If the direct reaction between N(V) and substrate is significant, then the reaction will not be autocatalytic.

Although one may point to features shared by nearly all autocatalytic substrates, there are several ways in which these reactions differ significantly from one another. Some intermediates (e.g., $FeNO^{2+}$) are resistant to oxidation by NO_2, while others (e.g., $NOSCNH^+$) are quite reactive. It does not appear possible to predict *a priori* the final oxidation state(s) of the reduced N(V).

One-electron reductants such as Fe^{2+} may react with NO_2 to produce HNO_2 in a single step. Two-electron reductants probably prefer to attack N_2O_4, abstracting an oxygen from it to form N_2O_3, which then hydrolyzes to $2HNO_2$. These plausible notions may be formulated as a general mechanistic scheme for autocatalytic nitric acid oxidations, where R′ and R are one- and two-electron reductants and R'^+ and RO are their respective oxidized forms:

$$H^+ + NO_3^- + HNO_2 \begin{array}{ll} \nearrow\!\!\!\swarrow N_2O_4 + H_2O & (29a) \\ \searrow\!\!\!\nwarrow 2NO_2 + H_2O & (29b) \end{array}$$

$$\begin{tikzcd} N_2O_4 + R \arrow[r] & N_2O_3 + RO \arrow[d, shift left] \arrow[d, phantom, "+\ H_2O"', shift right=12] \\ & 2HNO_2 \arrow[u, shift left] \end{tikzcd} \qquad (30a)$$

$$2\{NO_2 + R' + H^+ \rightarrow HNO_2 + R'^+\} \qquad (30b)$$

There are many possible further reactions which may make the kinetics of a particular reaction more complex. Further reduction of HNO_2 may follow (e.g., Fe^{2+}, NH_2OH), nitrite esters (e.g., $NOSCNH^+$) may be formed, or quite specific effects (e.g., $FeNO^{2+}$ formation) may occur. Calculations in progress indicate that the kinetic features of the Br^- and NH_2OH oxidations can also be described within this common formulation.

One difficulty in analyzing these reactions is that they take place only at rather high ionic strength and acidity. It is possible to separate the influence of $[H^+]$ and $[NO_3^-]$[19,20]; the oxidation can proceed at nitrate concentrations as low as 0.2 M, but only if the acidity is increased considerably. In all cases, the ionic strength is well out of the range of applicability of Debye–Hückel theory. Acidity functions may be used in dealing with the nitric acid concentrations. In some cases[20,21] reasonably good agreement between calculation and experiment was obtained simply by using analytical H^+ and NO_3^- concentrations. It will be a challenge to any proposed mechanism to explain the cutoff of autocatalytic behavior below ~ 2.5 M HNO_3 which occurs in many reactions, the maximum in the HNO_2 production at about 4 M HNO_3 in the hydroxylamine reaction, or a formal order in HNO_3 as high as ~ 13 in the oxidation of bromide.

We return to the question of the initial composition of nitric acid solutions. Our experience is that even the highest purity nitric acid purged thoroughly with nitrogen or argon contains some nitrogen compounds with oxidation states less than +5, and that these initial concentrations must be taken into account if reproducibility and quantitative agreement between simulation and experiment are to be obtained. Calculating the levels of these impurities from the equilibrium expressions for reactions (6) and (7) does not appear to be the most accurate procedure. We have instead adopted a more phenomenological approach.

One can add small amounts of HNO_2 to the initial mixture and observe the effect on the induction period. By extrapolation, one may then estimate the original "HNO_2 content." This technique gave good agreement for both the thiocyanate and hydroxylamine systems with an expression of the form

$$[HNO_2]_0 \sim 5 \times 10^{-8}\,[HNO_3]_0$$

Of course, the value of the proportionality constant may be different (and should be remeasured) for nitric acid of different origin.

Both experiments[21] and calculations (Table III) show that in the stoichiometrically negligible range between 10^{-7} M and 10^{-4} M added initial nitrite influences only the induction period and not the maximum reaction rate or the final product concentrations. The lack of effect on $r_{1/2}$ would suggest a formal zero order in HNO_2, which is far from the true situation. What happens is that once the autocatalytic stage begins, its rate is determined by the total $[HNO_2]$, the vast majority of which has been produced during the course of the reaction.

Two other factors deserve comment. First, initial addition of NO_2 or NO also shortens the induction period in much the same way as HNO_2.[19] This observation may be understood in terms of the interconversion of the different nitrogen oxidation states via reactions (5)–(8). Because of this phenomenon, it is probably advisable to refer to these reactions as "autocatalytic in nature" rather than to try to distinguish between reactions "autocatalytic in nitrite" and "autocatalytic in NO." A second related observation is that nitrite scavengers (azide, hydrazine, sulfamic acid) can lengthen the induction period by orders of magnitude. These compounds remove nitrite faster than it can react in the autocatalytic sequence. Their effect can be overcome by adding a sufficient excess of nitrite. This approach was utilized to initiate the traveling waves described earlier.[45]

POSSIBILITIES FOR OSCILLATION

As noted in the Introduction, our initial interest in autocatalytic nitric acid oxidations was sparked by the notion that these systems might be modified, like a number of other autocatalytic reactions,[4] to generate chemical oscillation in a CSTR. According to the cross-shaped phase diagram model,[3] an autocatalytic reaction which exhibits bistability may be converted to an oscillatory one by addition of an appropriate feedback species. However, the theory requires that the feedback reaction be much slower than the relaxation of the bistable subsystem to its steady states. Unfortunately, in the nitric acid oxidations this relaxation proceeds relatively slowly.

We have investigated a wide range of species as possible feedback reactants in conjunction with both the HNO_3–Fe(II) and the HNO_3–SCN^- reactions in the CSTR. Reductants have included sulfite, oxalic acid and methanol, while permanganate, chromate, persulfate and molybdate have been tried as oxidants. In addition, hydrogen peroxide, vanadium(IV), formaldehyde and nitrite, which may either reduce HNO_3 or oxidize the substrate, have been employed. In all cases, the feedback reaction has proved to be too rapid to generate oscillation.

The most promising results, shown in Fig. 7, were obtained with H_2O_2. As $[H_2O_2]$ is increased, the region of bistability narrows,

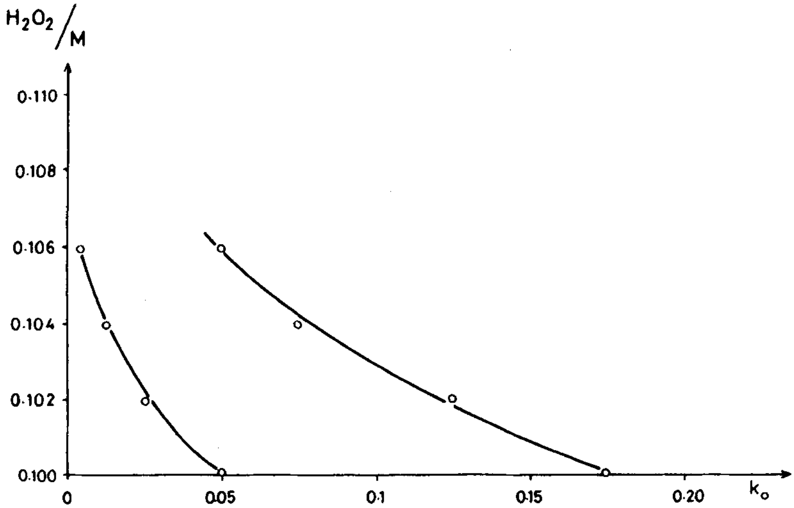

FIGURE 7 Phase diagram for the HNO_3–Fe(II)–H_2O_2 system in a CSTR. Fixed parameters: $[HNO_3]_0$ = 2 M, $[Fe(II)]_0$ = 0.24 M, T = 25 °C. k_0 is reciprocal residence time in s^{-1}.

as it should[3] if oscillation is to occur. Unfortunately instead of the region shrinking to zero width at a critical point, as observed in systems where oscillation appears, the two bistable states join smoothly and the system simply becomes monostable. With most other feedback species, increasing the feedback concentration broadened the range of bistability, dimming hopes for oscillation.

It may be instructive to compare the major kinetic features of bromate and nitric acid autocatalytic oxidations, since the former have been among the most fruitful sources of chemical oscillators.[9] There are several important similarities. In both cases the first step involves the conproportionation of the +5 and +3 oxidation states to produce two molecules in the +4 state. These +4 species then oxidize the substrate, while being reduced to the +3 state. This step is the source of autocatalysis in both the bromate and the nitric acid systems. A third step, formally a disproportionation of the +3 state, can also take place. In the case of bromate this reaction leads to the +5 (BrO_3^-) and +1 (HOBr) states, while with nitric acid the products are the +4 (NO_2) and +2 (NO) states.

The rate constants for the best studied substrates of each type are given in Table IV.

TABLE IV

Rate constants for nitrate and bromate oxidations

$NO_3 + H^+ + HNO_2 = 2NO_2 + H_2O$	1.5×10^{-2} M^{-1} s^{-1}	1×10^8 M^{-1} s^{-1}
$BrO_3 + H^+ + HBrO_2 = 2BrO_2 + H_2O$	1.0×10^4 M^{-1} s^{-1}	2×10^7 M^{-1} s^{-1}
$NO_2 + Fe^{2+} = HNO_2 + Fe^{3+}$	3.1×10^4 M^{-1} s^{-1}	6.5×10^{-4} M^{-1} s^{-1}
$BrO_2 + Ce^{3+} + H^+ = HBrO_2 + Ce^{4+}$	6.5×10^5 M^{-2} s^{-1}	2.4×10^7 M^{-1} s^{-1}
$2HNO_2 = NO^+ NO_2 + H_2O$	5.8 M^{-1} s^{-1}	2×10^7 M^{-1} s^{-1}
$2HBrO_2 = BrO_3 + HOBr + H^+$	4×10^7 M^{-1} s^{-1}	2.1×10^{-10} M^{-2} s^{-1}

There is a significant difference ($\sim 10^6$) in the rate constants for the initial nitrate and bromate oxidation steps. Neither NO_2 nor BrO_2 accumulates during the reaction, since they are rapidly reduced by the substrate. The acceleration of the autocatalytic process is controlled in nitric acid systems by the slowness of the first step, while the bromate autocatalysis is regulated by the rapid disproportionation of $HBrO_2$, an almost negligibly slow process in the case of HNO_2. It is this difference in the stage at which the autocatalytic process is contained that appears to account for the relatively sluggish nature of HNO_3 oxidations and the failure to find a feedback species slow enough to produce oscillation.

Acknowledgments

This work was supported by the National Science Foundation (CHE 8204085 and CHE 8419949) and by a U.S.-Hungarian cooperative grant (INT 8217658) from the NSF and the Hungarian Academy of Sciences. We thank Dorothy Rona for assistance with several of the experimental studies and K. Kustin, M. Orbán and M. T. Beck for stimulating discussions.

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