

Kinetics of oxidation of nitrogen compounds by cerium(IV)

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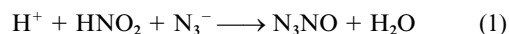
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The kinetics of oxidation by Ce^{IV} in sulfuric acid of hydrazine, hydroxylamine, nitrous acid, hydrazoic acid and of an intermediate involved in the nitrite/hydrazine reaction has been examined under a uniform set of conditions. Reaction proceeds through the free base form of the nitrogen substrate, probably by an inner-sphere mechanism, with a reactivity sequence N₂H₄ > NH₂OH > N₃⁻ > NO₂⁻. An intermediate in the hydrazine/nitrous acid reaction, NH₂N=NOH, is also oxidised by Ce^{IV} in a Ce^{IV}/HNO₂/N₂H₅⁺ system. For the Ce^{IV}/HNO/HN₃ system there is a much larger consumption of oxidant than can be accounted for by the separate oxidations of nitrite and azide. An additional pathway is proposed, probably involving NNN-O-N=O, formed by combination of azide and nitrogen dioxide radicals.

The present study began as an attempt to detect intermediates in various inorganic N-nitrosations by reaction with Ce^{IV} using a kinetic approach. In the analysis of an aqueous solution of NaNO₂ + NaN₃ in NaOH the nitrite ion was measured spectrophotometrically at 355 nm, and it was hoped to determine the total nitrite + azide volumetrically by reaction with an excess of cerium(IV) ion in sulfuric acid, and back titration of the residual oxidant by standardised iron(II) ion. As nitrite and azide react together in acid solution, eqns. (1) and (2), it was



necessary to check whether losses by such a reaction, which should lead to a *reduced* consumption of Ce^{IV}, were significant. When standard solutions of NaNO₂ + NaN₃ were analysed it was found that the consumption of cerium(IV) ion was actually much *greater* than that calculated from the known initial concentrations. This raised the possibility that Ce^{IV} was reacting with an intermediate, nitrosyl azide, in the nitrite/azide reaction.

The classic work of Clusius and Effenberger¹ using ¹⁵N tracer showed that the nitrite/azide reaction probably proceeded *via* nitrosyl azide, a result consistent with the general pattern of electrophilic reactions of nitrous acid² which commonly involve the formation of nitrosyl compounds such as ONCl, ONBr, ONSCN, *etc.* The decomposition reaction (2) is too fast for it to be observed directly by stopped-flow, but it was hoped to trap it by reaction with Ce^{IV}. The work was extended to see if intermediates in other inorganic N-nitrosation reactions could be detected. One advantage of the kinetic approach was that it provided relative reactivities of a number of compounds towards Ce^{IV} under a standard set of conditions. There have been previous studies of the kinetics of the cerium(IV) oxidation of inorganic nitrogen compounds, but reaction conditions have varied considerably.

Experimental

Materials

All chemicals used were AnalaR materials (BDH) with the exception of N₂H₅HSO₄ which was an Aldrich product. They were used without further purification.

Kinetics

Fast reactions were followed on a Canterbury SF 3A stopped-flow instrument with a data collection system. Measurements were made at 418 nm, calibrating with a holmium filter.

Titrimetric analyses for Ce^{IV}

In these experiments a 5 cm³ aliquot of Ce^{IV} in sulfuric acid in a 25 cm³ conical flask was vigorously stirred using a magnetic follower. An equal volume of NaNO₂ + NaN₃ solution was pipetted into the stirred solution, and there was a rapid evolution of gas. A clean dry 1 cm spectrophotometer cell was quickly filled from the solution in the conical flask and the absorbance measured at a pre-determined wavelength in a UNICAM 8625 spectrometer. It was essential to make this measurement as quickly as possible to avoid errors due to bubbles of liberated gas sticking to the cell wall in the light beam. The solution was then tipped back into the conical flask which was replaced on the magnetic stirrer. After a short interval, typically 30–60 s, the cell was refilled and the absorbance remeasured. This was repeated over a period of minutes until no further decrease in absorbance was observed. Finally, the solution was titrated with standardised ammonium iron(II) sulfate, using ferroin as an indicator. In experiments where a nitrate analysis was planned the excess of Ce^{IV} was titrated to a colourless end-point with standard sodium oxalate solution. These experiments were carried out at ambient temperatures, 21–22 °C.

Results

Kinetic studies

Stopped-flow spectrophotometry was used to study the kinetics of reaction of Ce^{IV} with HNO₂, HN₃, N₂H₅⁺, NH₃OH⁺ and NH₂SO₃H by following the decrease in absorbance, *A*, due to Ce^{IV} at 418 nm. All reactions were followed with one reagent in large excess over the other and gave excellent first order kinetics over at least three half-lives with plots of ln (*A* - *A*_∞) versus time, yielding rate constants *k*₁/s⁻¹. Average standard deviations for repeat runs were ±0.7%. All reactions were run in 0.725 mol dm⁻³ sulfuric acid at 25 °C. From the results of Robertson and Dunford³ this corresponds to [H⁺] = 0.929 mol dm⁻³ with a formal ionic strength of 1.13 mol dm⁻³.

Table 1 Kinetics of reaction of Ce^{IV} with HNO₂, HN₃ and NH₃OH⁺ in 0.725 mol dm⁻³ sulfuric acid at 25 °C

10 ² [HNO ₂]/mol dm ⁻³	5	4	3	2	1
k ₁ /s ⁻¹	18.2	15.1	11.4	7.36	3.65
10 ² [HN ₃]/mol dm ⁻³	5	4	3	2	1
k ₁ /s ⁻¹	115	88.7	65.3	43.3	20.9
10 ² [N ₂ H ₅ ⁺]/mol dm ⁻³	5	4	3	2	1
10 ² k ₁ /s ⁻¹	67.5	52.8	40.5	27.1	13.9

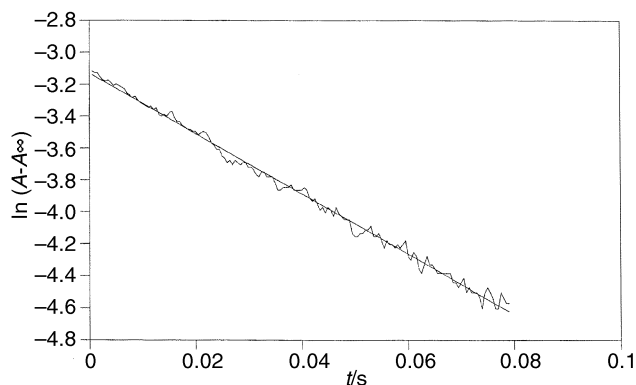
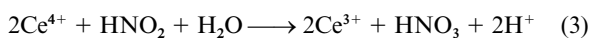


Fig. 1 First order plot for reaction of Ce^{IV} with an excess of HNO₂ at 25 °C, 10⁴[Ce^{IV}] = 5, 10²[HNO₂] = 5, [H₂SO₄] = 0.725 mol dm⁻³.

Reaction with HNO₂. This is a well established reaction for the volumetric estimation of nitrites; the stoichiometry is shown in eqn. (3). Reaction with a large excess of nitrous acid gave

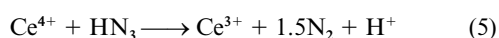


values of k_1 directly proportional to [HNO₂] yielding rate law (4) with $k_2 = 370 \pm 5.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Data are set out in

$$-d[\text{Ce}^{\text{IV}}]/dt = k_2[\text{Ce}^{\text{IV}}][\text{HNO}_2] \quad (4)$$

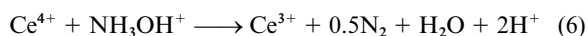
Table 1 and a typical run is shown in Fig. 1. Experiments with a large excess of Ce^{IV} gave $k_2 = 386 \pm 12 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reaction with HN₃. This is also a reaction used as a standard volumetric procedure with the 1:1 stoichiometry of eqn. (5).



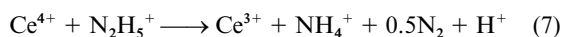
The kinetics was again studied with a large excess of azide, and k_1 found to be directly proportional to [HN₃] (Table 1) giving a second order rate constant $k_3 = 2280 \pm 39 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. When an excess of Ce^{IV} was used, $k_3 = 2211 \pm 29 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reaction with NH₃OH⁺. This has been studied in detail by Waters and Wilson⁴ who observed second order kinetics, k_4 , first order with respect to each reactant concentration. For an excess of hydroxylamine the stoichiometry is shown in eqn. (6).



Under our standard conditions with an excess of NH₃OH⁺, and assuming the kinetic form found by Waters and Wilson, we found $k_4 = 111 \pm 1.7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reaction with N₂H₅⁺. Morrow and Sheeres⁵ have shown that for the cerium(IV) oxidation of hydrazine in perchloric acid the stoichiometry is dependent upon the oxidant:reductant ratio. For an excess of hydrazine the reaction is shown in eqn. (7). We



have studied the reaction in a large excess of hydrazine and again find k_1 directly proportional to [N₂H₅⁺] yielding a second order rate constant $k_5 = 13.4 \pm 0.13 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which compares with a value⁵ of $9.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in 1 mol dm^{-3} perchloric acid. These are stoichiometric rate constants based upon the total concentration of hydrazine species. If there is significant protonation to N₂H₆²⁺ then these values need to be corrected. Stanbury⁶ has reviewed literature data and suggested a pK_1 for N₂H₆²⁺ of -0.5 which converts our k_5 from 13.4 into $17.4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (for N₂H₅⁺ as the hydrazine species). Margerum and Jia⁷ have recently measured pK_1 and find a value of 0.23 at 1 mol dm^{-3} ionic strength which gives a corrected k_5 of $35.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reaction with NH₂SO₃H. There was no detectable reaction on the stopped-flow timescale.

Acidity dependence of the above reactions

As both oxidant and reductant can exist in conjugate acid–base forms it was necessary to know the acidity dependence of k_1 . In sulfuric acid Ce^{IV} exists as a mixture of Ce⁴⁺, [Ce(OH)]³⁺, [Ce(SO₄)]²⁺, Ce(SO₄)₂ and [Ce(SO₄)₃]²⁻. At sufficiently high concentrations of Ce^{IV} dimeric species exist. Changes in the sulfuric acid concentration may thus vary the proportions of different complexes present as well as varying [H⁺]. Furthermore, the formal ionic strength in our system is outside the range for which activity coefficient corrections can be calculated. Hanna *et al.*⁸ suggested a method of preparing a solution of HClO₄ + NaClO₄ + Na₂SO₄ of a given ionic strength, in which [H⁺] can be varied but [SO₄²⁻] is kept constant. This should keep the relative concentrations of the various sulfate complexes constant. We have used Hanna's method to compare rates at [H⁺] = 0.7 and 0.2 mol dm⁻³. For a 3.5 fold decrease in [H⁺] k_2 increased by a factor of 3.1, k_3 by 3.0, k_4 by 3.1 and k_5 by 3.4. If a correction for double protonation of hydrazine is made Stanbury's value for the pK_a leads to a corrected factor of 2.9 for k_5 while Margerum's value reduces it to 2.1.

Kinetics of reaction in a mixed Ce^{IV}/HNO₂/N₂H₅⁺ system

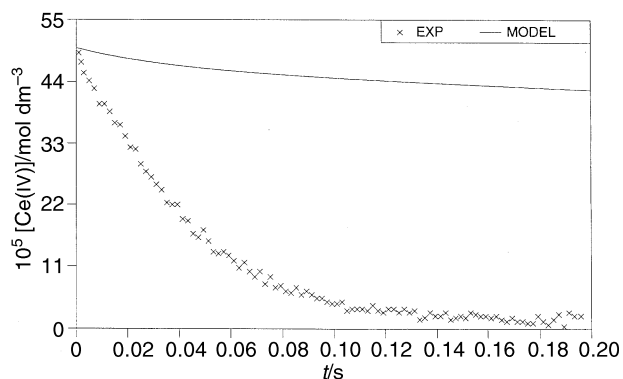
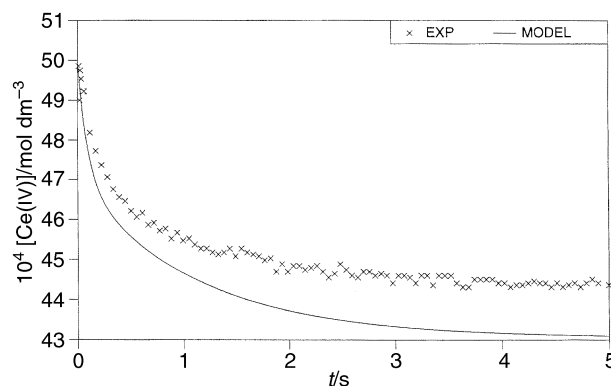
The reaction between nitrous acid and hydrazine follows kinetic law (8), an initial N-nitrosation to form NH₂NHNO (or a

$$-d[\text{HNO}_2]/dt = k_6[\text{H}^+][\text{HNO}_2][\text{N}_2\text{H}_5^+] \quad (8)$$

conjugate acid thereof), followed by a rapid tautomerisation to form an intermediate NH₂N=NOH that can be detected spectrophotometrically.⁹ To investigate whether this intermediate would react with Ce^{IV} one reservoir of the stopped-flow apparatus contained NaNO₂ + N₂H₄ while the other contained Ce^{IV} in sulfuric acid. Monitoring the nitrite ion peak at 355 nm for the reservoir solution showed no change in absorbance over a period of hours confirming the stability in the absence of acid. Conditions were chosen so that the known rate of (8) was much faster than the rate of the Ce^{IV}/HNO₂ reaction so that on rapid mixing the nitrite/hydrazine mixture was acidified and the intermediate NH₂N=NOH formed almost quantitatively. Thus, for $0.725 \text{ mol dm}^{-3}$ sulfuric acid and $[\text{N}_2\text{H}_5^+]_0 = 0.035 \text{ mol dm}^{-3}$ at 25 °C the rate of reaction (8) is $-d[\text{HNO}_2]/dt = 26.7[\text{HNO}_2]$ whereas for reaction with $5 \times 10^{-4} \text{ mol dm}^{-3}$ Ce^{IV} the rate is $-d[\text{HNO}_2]/dt = 0.092[\text{HNO}_2] \text{ mol dm}^{-3} \text{ s}^{-1}$. Thus nearly all of the nitrous acid reacts with the hydrazine and almost none with Ce^{IV}. On mixing there was a rapid decrease in [Ce^{IV}], much faster than the known rate of the Ce^{IV}/hydrazine reaction as shown in Fig. 2. The continuous line represents the predicted rate of consumption of Ce^{IV} if the only processes are the Ce^{IV}/hydrazine, Ce^{IV}/nitrous acid and nitrous acid/hydrazine reactions. From the half-lifetimes for the decrease in absorbances an

Table 2 Stoichiometric data on the reaction of excess of Ce^{IV} with sodium nitrite + sodium azide

Run	[Ce ^{IV}] ₀ / mol dm ⁻³	[NO ₂ ⁻] ₀ / mol dm ⁻³	[N ₃ ⁻] ₀ / mol dm ⁻³	[Ce ^{IV}] _∞ / mol dm ⁻³	R	k/s ⁻¹
1	0.125	0.025	0.025	0.0005	1.66	
2	0.125	0.025	0.025	0.0007	1.66	0.016
3	0.083	0.033	0.000	0.01613	2.02	
6	0.0625	0.000	0.050	0.0135	0.98	
7	0.125	0.025	0.025	0.0008	1.66	
8	0.125	0.0125	0.0125	0.0626	1.66	0.018
9	0.125	0.0083	0.0083	0.0841	1.64	0.018
10	0.125	0.0083	0.0083	0.0850	1.60	0.017
12	0.125	0.0166	0.0166	0.0418	1.66	0.013
13	0.125	0.0083	0.0083	0.0843	1.63	0.015
18	0.0125	0.0025	0.0025	0.000	>1.66	
19	0.0166	0.0016	0.0016	0.00862	1.61	0.014
20	0.0227	0.0091	0.00	0.004218	2.04	
21	0.0125	0.00125	0.00125	0.00638	1.63	0.013
22	0.125	0.01	0.02	0.0596	1.64	
23	0.083	0.0133	0.0266	0.000	>1.56	0.012
24	0.0125	0.02	0.01	0.0474	1.55	0.013
25	0.125	0.025	0.00625	0.0505	1.32	0.015
26	0.125	0.025	0.00625	0.0554	1.25	
27	0.125	0.00625	0.025	0.0692	1.49	
28	0.125	0.00625	0.025	0.0697	1.47	
34	0.005	0.0005	0.0005	0.00227	1.82	
36	0.00469	0.000625	0.000625	0.00136	1.77	

**Fig. 2** Reaction of Ce^{IV} with N₂H₅⁺ + HNO₂ at 25 °C, 10⁴[Ce^{IV}] = 5, 10⁵[N₂H₅⁺] = 35, 10³[HNO₂] = 5, [H₂SO₄] = 0.725 mol dm⁻³.**Fig. 3** Reaction of Ce^{IV} with HN₃ + HNO₂ at 25 °C, 10³[Ce^{IV}] = 5, 10⁴[HN₃] = 2, 10⁴[HNO₂] = 3, [H₂SO₄] = 0.725 mol dm⁻³. x, Experimental points; full line, computed model.

apparent order of reaction with respect to [Ce^{IV}] can be calculated and was found to be 0.88 for [N₂H₅⁺]₀ = 0.035 decreasing to 0.81 for [N₂H₅⁺]₀ = 0.0075 mol dm⁻³. When [HNO₂]₀ was varied it was found that $-(d[\text{Ce}^{\text{IV}}]/dt)_0$ was proportional to [HNO₂]₀.

Kinetics of the Ce^{IV}/HNO₂/HN₃ systems

The cerium(IV) consumption experiments that led to the present work involved relatively high concentrations of reagents, *e.g.* [Ce^{IV}] 0.125, [NaNO₂] 0.025 and [NaN₃] 0.025 mol dm⁻³. At these concentrations the rates of reaction were too fast to be studied by our stopped-flow. Thus for the Ce^{IV}/HN₃ reaction $t_{1/2} \approx 2.5$ ms, considerably faster than our mixing time. Furthermore, vigorous gas evolution made it impossible to get good absorbance *vs.* time traces. Reasonable curves could be obtained for [Ce^{IV}] = 0.005 mol dm⁻³ with correspondingly lower concentrations of azide and nitrite and a typical trace is shown in Fig. 3. There was a rapid initial decrease in absorbance followed by a very much slower decay. The experimental points, shown as crosses, are compared with the full line calculated from the known rates¹⁰ of reactions (1), (3) and (5). These results contrast with those from experiments in which nitrite and azide were in large excess over cerium where the curve of [Ce^{IV}] against time was in close agreement with that calculated.

Reaction of the Ce^{IV}/HNO₂/NH₃OH⁺ and the Ce^{IV}/HNO₂/NH₂SO₃H systems

These experiments were unsuccessful because the reaction of hydroxylamine with nitrous acid is relatively slow¹¹ and we were unable to obtain any evidence for reaction of Ce^{IV} with any of the postulated intermediates in the HNO₂/NH₃OH⁺ reaction. The nitrite reacted preferentially with Ce^{IV}. Sulfamic acid is, like hydrazine, an excellent trap for nitrous acid^{12,13} and it was easy to set up conditions where the nitrite reacted almost 100% with NH₂SO₃H. However, in the three reactant system there was no consumption of Ce^{IV}; either the expected intermediates ON·NHSO₃H or HON=NSO₃H were resistant to oxidation or they decomposed too rapidly.

Stoichiometric experiments on the Ce^{IV}/HNO₂/HN₃ system

Most of this work consisted of determining the residual [Ce^{IV}] when a mixture of NaNO₂ + NaN₃ was treated with an excess of oxidant. The results are summarised in Table 2 where the column headed *R* represents the ratio of Ce^{IV} consumed to the value expected on the basis of eqns. (3) and (5), as shown in (9). In some of these experiments the final value of [Ce^{IV}] is

$$R = ([\text{Ce}^{\text{IV}}]_0 - [\text{Ce}^{\text{IV}}]_{\infty}) / (2[\text{NO}_2^-]_0 + [\text{N}_3^-]_0) \quad (9)$$

very small, e.g. 1, 2, 7, while in others the excess of oxidant was much larger, e.g. 9, 10, 13. The high consumption of Ce^{IV} is still observed at lower concentrations of oxidant, comparable to those used in the kinetics experiment. The large increase in consumption of Ce^{IV} when azide + nitrite are oxidised is clear cut.

Under our conditions, with an excess of Ce^{IV}, the only stable nitrogen compounds are N₂, N₂O and NO₃⁻; these are also the products for reactions (1) + (2), (3) and (5). The two gases have been confirmed by mass spectrometry, and nitrate has been determined by reduction to nitrite with Cd(s), followed by diazotisation and coupling. Some results are given in Table 3.

In these experiments we also obtained some kinetic data, monitoring the change in absorbance *A* in the later stages of reaction. The results fitted a first order rate law [$-dA/dt = k_7(A - A_\infty)$], k_7/s^{-1} and the rate constants are shown in the last column of Table 2. These k_7 values are based on only a few points, and the accuracy was reduced by problems due to evolution of gas bubbles. We cannot detect any trend in the values of k_7 . This relatively slow disappearance of Ce^{IV} in the final stages of reaction was also observed in an experiment when titrimetric analysis was used to determine [Ce^{IV}].

Discussion

The variation of k_1 with [H⁺] suggests a rate law with a 1/[H⁺] dependence. Morrow and Sheeres⁵ examined the oxidation of hydrazine by Ce^{IV} in perchloric acid, 0.5–3 mol dm⁻³, and found k_1 directly proportional to 1/[H⁺]. Studies on the cerium(IV) oxidation of hydroxylamine and of nitrous acid in sulfuric acid^{4,14} showed a rate that increased as [H₂SO₄]_{total} decreased, but here the interpretation may be complicated by the varying degrees of complexation by the sulfate ion. The obvious explanation of the acidity dependence is that a conjugate base species, either of oxidant or reductant, is involved. In the first case, this would imply [Ce(OH)]³⁺ reacting with the reductant in its conjugate acid form red H⁺. Morrow and Sheeres have proposed such a mechanism involving hydrogen transfer. It is unlikely that this could be the pattern for all four reductants. The (E°)_{Hred} values for red⁺ + H⁺ + e → Hred⁺ make N₂H₅⁺ and NH₃OH⁺ the two most powerful reductants, yet they have the lowest reactivities. A more direct point against the [Ce(OH)]³⁺ interpretation is that in 1 mol dm⁻³ perchloric acid a substantial fraction of Ce^{IV} should exist as the hydroxo complex, whereas in our system competitive complexation by sulfate ion reduces [Ce(OH)]³⁺ to about 0.02% of total cerium (based on Hardwick and Robertson's formation constant³ data). However, the stoichiometric second order rate constant for 0.94 mol dm⁻³ H⁺ in sulfuric acid is similar to the value for 1 mol dm⁻³ perchloric acid!

The alternative interpretation is that the conjugate base species NO₂⁻, N₃⁻, NH₂OH and N₂H₄ react with the oxidant.

Table 3 Yields of nitrate for oxidation by 0.125 mol dm⁻³ Ce^{IV}

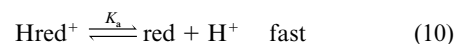
[NO ₂ ⁻] ₀ /mol dm ⁻³	0.025	0.0333	0.0166	0.01
[N ₃ ⁻] ₀ /mol dm ⁻³	0.025	0.0166	0.0333	0.04
[NO ₃ ⁻] _∞ /mol dm ⁻³	0.034	0.044	0.0286	0.0217

Table 4 Redox data on nitrogen substrates

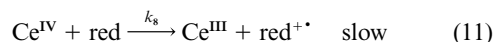
Hred ⁺	<i>n</i>	$k_n/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	pK_a	$k_8/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	(E°) _{red} /V	(E°) _{Hred} /V
HNO ₂	2	370	3.00 ^a	3.5×10^5	1.04 ^b	1.23
HN ₃	3	2280	4.44 ^c	5.9×10^7	1.33 ^b	1.61
NH ₃ OH ⁺	4	111	6.06 ^d	1.2×10^8	0.42 ^e	0.77
N ₂ H ₅ ⁺	5	13.4	7.87 ^f	9.3×10^8	0.69 ^g	1.16

^a Ref. 15. ^b Ref. 22. ^c Ref. 16. ^d Ref. 17. ^e Ref. 21. ^f Ref. 18. ^g Ref. 6.

Writing this in the simplest form of a second order process with (11) as the rate-determining step, and leaving aside the question



of whether (11) is better written as an inner or an outer sphere reaction, one obtains rate law (12).



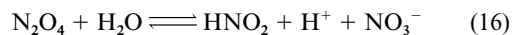
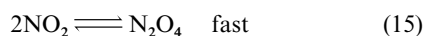
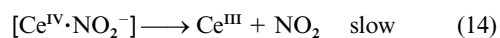
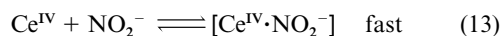
$$-d[\text{Ce}^{\text{IV}}]/dt = (k_8/K_a)[\text{Ce}^{\text{IV}}][\text{Hred}^+]/[\text{H}^+] \quad (12)$$

The steps by which red⁺ radical species such as N₂H₄⁺⁺, NH₂OH⁺⁺ are converted into the final products are assumed to be rapid and have been discussed^{4,6} by other workers. Values of k_8 are listed in Table 4. Values for the pK_a in 0.725 mol dm⁻³ sulfuric acid are not available, and we have used literature figures^{15–18} for 1 mol dm⁻³ NaClO₄. This gives the two strongest reducing agents the largest k_8 values with N₂H₄ having a bimolecular rate constant not too far below the encounter limit. This raises the question of the nature of the oxidant. In our system calculations indicate that approximately 92% is present as [Ce(SO₄)₃]²⁻, 8% as Ce(SO₄)₂, and 0.07% as [Ce(SO₄)₂]²⁺ with very small amounts of [Ce(OH)]³⁺, Ce⁴⁺ and [Ce₂(OH)₂]⁶⁺. Previous workers have usually sought to implicate a particular cerium(IV) complex as the oxidant, and it is tacitly assumed that the more sulfate ligands bound to cerium the lower is the reactivity, although E° data for the Ce^{IV}–Ce^{III} couple are reported¹⁹ to be almost constant from 0.5 to 4 mol dm⁻³ sulfuric acid. The value of k_8 for N₂H₄ is only a factor of ten below the encounter limit, and as we calculate ca. 8% of the cerium is present as Ce(SO₄)₂ this would be consistent with a diffusion controlled reaction between Ce(SO₄)₂ and N₂H₄. Presumably, the less sulfated complexes would also react at every encounter. Mishra and Gupta²⁰ also suggested Ce(SO₄)₂ as the active species. However, we are sceptical that such calculations are accurate enough to exclude some contribution from [Ce(SO₄)₃]²⁻, and would merely claim that most of the cerium(IV) complexes react with N₂H₄ at close to the encounter rate.

The same problem arises with the other reductants. Waters and Wilson⁴ examined the oxidation of hydroxylamine in 3–9 mol dm⁻³ sulfuric acid and suggested an inner-sphere mechanism involving Ce(SO₄)₂·NH₂OH, while Treindl and Viludevá¹⁴ working in 0.5–5 mol dm⁻³ sulfuric acid suggested [Ce(SO₄)·NH₂OH]²⁺. We doubt whether over such wide ranges of sulfuric acid concentration it is possible to calculate the variation of the relative proportions of the various complexes with sufficient accuracy to identify a particular Ce^{IV}/sulfate complex as the only active species.

The k_8 values for NH₂OH and N₃⁻ are very similar, ca. 10⁸ dm³ mol⁻¹ s⁻¹, and are significantly below the encounter limit. Hydroxylamine is a much stronger reducing agent, (E°)_{red} for red⁺ + e → red being 0.42 V²¹ compared to 1.33 V for azide,²² but this may be offset by a much lower self-exchange constant²³ (log $k_{11} = -12.3$ compared to +4.7 for azide). For the oxidation of nitrous acid to nitric acid we have a two equivalent change. The value of E° for the NO₂–NO₂⁻ couple²² 1.04 V, is lower than for the Ce^{IV}–Ce^{III} couple of 1.45 V, so

the oxidation of NO_2^- to NO_2 is reasonable. For the $\text{NO}_2^+ - \text{NO}_2$ couple²² E° is 1.51 V, and the oxidation involves a large geometry change from bent to linear. Swarski *et al.*,²⁴ in the course of a study of the radiation chemistry of sodium nitrate solution in the presence of Ce^{IV} , studied the $\text{Ce}^{\text{IV}}/\text{HNO}_2$ reaction. They proposed the mechanism in eqns. (13)–(16). We see no reason to



modify this. The rate data of Swarski *et al.* when interpolated at $[\text{H}_2\text{SO}_4] = 0.725 \text{ mol dm}^{-3}$ gave $k_2 = 331 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in reasonable agreement with our results, assuming that their room temperature (unspecified) was somewhat below 25 °C. We have considered the possibility of an outer-sphere mechanism. Using the simpler form of the Marcus equation²⁵ without work terms one can use $(E^\circ)_{\text{red}}$ ²² and the self-exchange constants²³ for $\text{red}/\text{red}^{+}$ combined with the k_8 values for total Ce^{IV} to calculate apparent 'self-exchange constants' for $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ in 0.725 mol dm^{-3} sulfuric acid. Such calculations showed no sort of self-consistency, giving values/ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ of $10^{5.6}$ (NO_2^-), $10^{9.2}$ (N_3^-) and $10^{15.1}$ (NH_2OH). These can be compared with a literature value²⁶ of $4.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ in 0.4 mol dm^{-3} sulfuric acid at 0 °C. We conclude that these oxidations proceed by an inner sphere mechanism.

The $\text{Ce}^{\text{IV}}/\text{HNO}_2/\text{N}_2\text{H}_5^+$ system

The observed rate of consumption of Ce^{IV} is much faster than the rate expected for the relatively slow Ce^{IV} /hydrazine reaction as can be seen from Fig. 2. Comparison of the half-lifetimes shows that the rate of consumption of Ce^{IV} is very similar to that calculated for the rate of the hydrazine/nitrous acid reaction. For $[\text{N}_2\text{H}_5^+]_0 = 0.035$, $[\text{HNO}_2]_0 = 0.0025$, $[\text{Ce}^{\text{IV}}]_0 = 0.0005 \text{ mol dm}^{-3}$ successive half-lives for Ce^{IV} are 0.0318, 0.0282, 0.027 s which compare with calculated values for $\text{N}_2\text{H}_5^+/\text{HNO}_2$ of 0.027, 0.028 and 0.029 s. An exact comparison is not to be expected because the calculated rate of the hydrazine/nitrous acid reaction was obtained from a study¹⁰ in perchloric acid, assuming that the rate in sulfuric acid would be the same at a given H_0 value. The results show that Ce^{IV} reacts rapidly with an intermediate in the hydrazine/nitrous acid reaction, $\text{NH}_2\text{N}=\text{NOH}$. There is a precursor to this species, the initial nitrosation product NH_2NHNO , and the possibility that Ce^{IV} reacts with this before it tautomerises to $\text{NH}_2\text{N}=\text{NOH}$ cannot be excluded. At lower concentrations of hydrazine the rate of cerium(IV) consumption is somewhat less. An approximate value for the rate constant k_8 based on the assumed eqn. (17) was obtained



by setting up a series of differential equations for $d[\text{Ce}^{\text{IV}}]/dt$, $d[\text{N}_2\text{H}_5^+]/dt$, $d[\text{HNO}_2]/dt$ and $d[\text{NH}_2\text{N}=\text{NOH}]/dt$ and integrating by the Gear method. A series of values for k_8 was tried and the best fit, shown in the figure, gave $k_8 \approx 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This fit is not perfect, and it may be that additional terms should be included in the numerical integration. The only literature report of any related process is a study by Gupta and co-workers²⁷ of the cerium(IV) reaction with hyponitrous acid $\text{H}_2\text{N}_2\text{O}_2$. Gupta suggested oxidation of $\text{HON}=\text{NOH}$ to $\text{HON}=\text{NO}^+$ followed by a further oxidation to the acid form of Angeli's salt, $\text{H}_2\text{N}_2\text{O}_3$ ($\text{HON}(\text{O})=\text{NOH}$) which breaks down to HNO_2 and HNO , which then undergoes further reaction to form N_2 , HNO_3 and N_2O . A similar pathway in our system

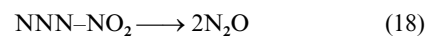
could yield $\text{NH}_2\text{N}(\text{O})=\text{NOH}$ which could yield $\text{NH}_2\text{NO} + \text{NOH}$ which would give $\text{N}_2 + 0.5\text{N}_2\text{O} + 1.5\text{H}_2\text{O}$. We have no evidence on this point.

The $\text{Ce}^{\text{IV}}/\text{HNO}_2/\text{HN}_3$ system

The stoichiometric results show clearly that there is a large excess consumption of Ce^{IV} over that expected for reactions (3) and (5). Solutions of Ce^{IV} in sulfuric acid are very stable, and losses by oxidation of water to O_2 are negligible. This was confirmed by a mass-spectrometric analysis. The concentration of nitrate ions formed is greater than the initial nitrite concentration, so some of the azido nitrogen must have been oxidised. We considered the possibility of mechanisms involving the known intermediate N_3NO formed in reaction (1) or the species $\text{NNN}-\text{NO}_2$ or $\text{NNN}-\text{O}-\text{N}=\text{O}$ that might be formed by combination of the radicals NO_2 and N_3 .

The rate of decomposition of nitrosyl azide, reaction (2), has been found by Goldstein and Czapski²⁸ to be $>10^6[\text{N}_3\text{NO}] \text{ mol dm}^{-3} \text{ s}^{-1}$, so an encounter controlled reaction with 0.125 mol dm^{-3} Ce^{IV} could possibly trap N_3NO before it decomposed to $\text{N}_2 + \text{N}_2\text{O}$. However, the rate of formation of N_3NO is very much less than the rates of cerium(IV) oxidation of HNO_2 and HN_3 under our conditions, so it seems unlikely that this can account for the excess consumption of oxidant. Thus mixing equal volumes of our stock solutions of Ce^{IV} and $\text{NaNO}_2 + \text{NaN}_3$, the calculated rates of reactions (5), (3) and (1) are 276, 48 and 0.7 mol $\text{dm}^{-3} \text{ s}^{-1}$ respectively.

The molecule nitryl azide, $\text{NNN}-\text{NO}_2$, has been made²⁹ by the reaction of NO_2^+ with N_3^- in organic solvents, and is markedly more stable than N_3NO . However, it decomposes to form dinitrogen monoxide, eqn. (18), and so although it may be



formed by radical combination it is unlikely to be responsible for the consumption of Ce^{IV} . The isomeric species $\text{NNN}-\text{O}-\text{N}=\text{O}$ could also be formed by radical combination, and has been postulated as an intermediate³⁰ to account for the products of the oxidation of hydrazoic acid by concentrated nitric acid. A fragmentation reaction such as (19) would produce



nitric oxide which should be readily oxidisable to NO^+ which would hydrate to $\text{HNO}_2 + \text{H}^+$. The simple form of the Marcus equation can be used to predict a bimolecular rate constant for an outer sphere oxidation of NO by Ce^{IV} of *ca.* $330 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Such a reaction would require 6 equivalents of Ce^{IV} to convert both NO molecules into nitrate and could readily account for excess consumption of oxidant.

To check whether this suggestion is reasonable we assumed that the rate constant of combination for N_3/NO_2 may be approximated as the geometric mean of the known^{31,32} combination rate constants of N_3/N_3 and NO_2/NO_2 . A steady state treatment based on the rates of formation and removal of N_3 and NO_2 leads to the prediction that the rate of combination of N_3/NO_2 is *ca.* 1/6 of the rate of N_3/N_3 (which is close to the encounter limit). Thus a reasonable assumption about the rate of combination of N_3 and NO_2 predicts the formation of a sizeable amount of the combined product, which may be, of course, a mixture of isomers. This is, therefore, a reasonable mechanism to account for the undoubted excess consumption of Ce^{IV} .

The final point to discuss is the relatively slow fading of the absorbance in the later stages of the run, which is very much slower than would be predicted from the stopped-flow kinetics. For example, in run 9, the half-lifetime for the consumption of nitrite is calculated to be *ca.* 0.02 s, and for the reaction of azide it should be even less. However, the absorbance changes were measured over a period of *ca.* 2 min, with a half-lifetime of

38.5 s. In run 12 the changes were observed over a 5 min time-scale. The most likely explanation is that we are observing a rate determining fragmentation of our postulated NNN-O-N=O species, followed by rapid oxidation of NO. It would be interesting to see if these effects were observed for the oxidation of mixtures of nitrite and azide by other powerful one equivalent oxidising agents. We also considered the possibility that this might be due to a shift in the monomer-dimer equilibrium for Ce^{IV} as the system equilibrated after the rapid consumption of oxidant. However, for reactions with nitrite alone as reductant, we did not observe this effect; it occurred for reaction in a system containing *both* nitrite and azide. The fact that the slow disappearance of Ce^{IV} in the final stages of reaction was also observed using titrimetric analysis also argues against this interpretation.

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