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Kinetics of oxidation of nitrogen compounds by cerium(IV)

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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 $N_2H_4 > NH_2OH > N_3^- > NO_2^-$. An intermediate in the hydrazine/nitrous acid reaction, $NH_2N{=}NOH$, is also oxidised by Ce^{IV} in a $Ce^{IV}/HNO_2/N_2H_5^+$ system. For the $Ce^{IV}/HNO/HN_3$ 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 $NaNO_2 + NaN_3$ 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

$$H^+ + HNO_2 + N_3^- \longrightarrow N_3NO + H_2O \qquad (1)$$

$$N_3NO \longrightarrow N_2 + N_2O \qquad (2)$$

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 $NaNO_2 + NaN_3$ 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 Effenberger[1] using ^{15}N tracer showed that the nitrite/azide reaction probably proceeded *via* nitrosyl azide, a result consistent with the general pattern of electrophilic reactions of nitrous acid[2] 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 $N_2H_5HSO_4$ 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 $NaNO_2 + NaN_3$ 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 HNO_2, HN_3, $N_2H_5^+$, NH_3OH^+ and NH_2SO_3H 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 $(A - A_\infty)$ *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 Dunford[3] 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 HNO_2, HN_3 and NH_3OH^+ 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
$10^2[N_2H_5^+]$/mol dm^{-3}	5	4	3	2	1
10^2k_1/s^{-1}	67.5	52.8	40.5	27.1	13.9

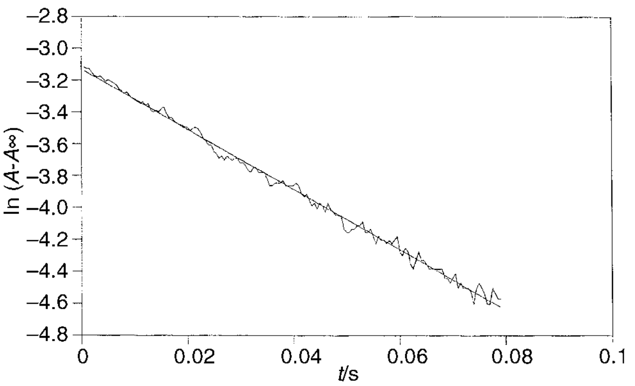

Fig. 1 First order plot for reaction of Ce^{IV} with an excess of HNO_2 at 25 °C, $10^4[Ce^{IV}] = 5$, $10^2[HNO_2] = 5$, $[H_2SO_4] = 0.725$ mol dm^{-3}.

Reaction with HNO_2. 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

$$2Ce^{4+} + HNO_2 + H_2O \longrightarrow 2Ce^{3+} + HNO_3 + 2H^+ \quad (3)$$

values of k_1 directly proportional to $[HNO_2]$ yielding rate law (4) with $k_2 = 370 \pm 5.5$ dm^3 mol^{-1} s^{-1}. Data are set out in

$$-d[Ce^{IV}]/dt = k_2[Ce^{IV}][HNO_2] \quad (4)$$

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

Reaction with HN_3. This is also a reaction used as a standard volumetric procedure with the 1 : 1 stoichiometry of eqn. (5).

$$Ce^{4+} + HN_3 \longrightarrow Ce^{3+} + 1.5N_2 + H^+ \quad (5)$$

The kinetics was again studied with a large excess of azide, and k_1 found to be directly proportional to $[HN_3]$ (Table 1) giving a second order rate constant $k_3 = 2280 \pm 39$ dm^3 mol^{-1} s^{-1}. When an excess of Ce^{IV} was used, $k_3 = 2211 \pm 29$ dm^3 mol^{-1} s^{-1}.

Reaction with NH_3OH^+. This has been studied in detail by Waters and Wilson[4] 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).

$$Ce^{4+} + NH_3OH^+ \longrightarrow Ce^{3+} + 0.5N_2 + H_2O + 2H^+ \quad (6)$$

Under our standard conditions with an excess of NH_3OH^+, and assuming the kinetic form found by Waters and Wilson, we found $k_4 = 111 \pm 1.7$ dm^3 mol^{-1} s^{-1}.

Reaction with $N_2H_5^+$. Morrow and Sheeres[5] 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

$$Ce^{4+} + N_2H_5^+ \longrightarrow Ce^{3+} + NH_4^+ + 0.5N_2 + H^+ \quad (7)$$

have studied the reaction in a large excess of hydrazine and again find k_1 directly proportional to $[N_2H_5^+]$ yielding a second order rate constant $k_5 = 13.4 \pm 0.13$ dm^3 mol^{-1} s^{-1}, which compares with a value[5] of 9.6 dm^3 mol^{-1} 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 $N_2H_6^{2+}$ then these values need to be corrected. Stanbury[6] has reviewed literature data and suggested a pK_1 for $N_2H_6^{2+}$ of −0.5 which converts our k_5 from 13.4 into 17.4 dm^3 mol^{-1} s^{-1} (for $N_2H_5^+$ as the hydrazine species). Margerum and Jia[7] 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 dm^3 mol^{-1} s^{-1}.

Reaction with NH_2SO_3H. 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 Ce^{4+}, $[Ce(OH)]^{3+}$, $[Ce(SO_4)]^{2+}$, $Ce(SO_4)_2$ and $[Ce(SO_4)_3]^{2-}$. 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 $HClO_4$ + $NaClO_4$ + Na_2SO_4 of a given ionic strength, in which $[H^+]$ can be varied but $[SO_4^{2-}]$ 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 $Ce^{IV}/HNO_2/N_2H_5^+$ system

The reaction between nitrous acid and hydrazine follows kinetic law (8), an initial N-nitrosation to form NH_2NHNO (or a

$$-d[HNO_2]/dt = k_6[H^+][HNO_2][N_2H_5^+] \quad (8)$$

conjugate acid thereof), followed by a rapid tautomerisation to form an intermediate $NH_2N{=}NOH$ that can be detected spectrophotometrically.[9] To investigate whether this intermediate would react with Ce^{IV} one reservoir of the stopped-flow apparatus contained $NaNO_2$ + N_2H_4 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}/HNO_2 reaction so that on rapid mixing the nitrite/hydrazine mixture was acidified and the intermediate $NH_2N{=}NOH$ formed almost quantitatively. Thus, for 0.725 mol dm^{-3} sulfuric acid and $[N_2H_5^+]_0 = 0.035$ mol dm^{-3} at 25 °C the rate of reaction (8) is $-d[HNO_2]/dt = 26.7[HNO_2]$ whereas for reaction with 5×10^{-4} mol dm^{-3} Ce^{IV} the rate is $-d[HNO_2]/dt = 0.092[HNO_2]$ mol dm^{-3} 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}	$[Ce^{IV}]_\infty$/ 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	

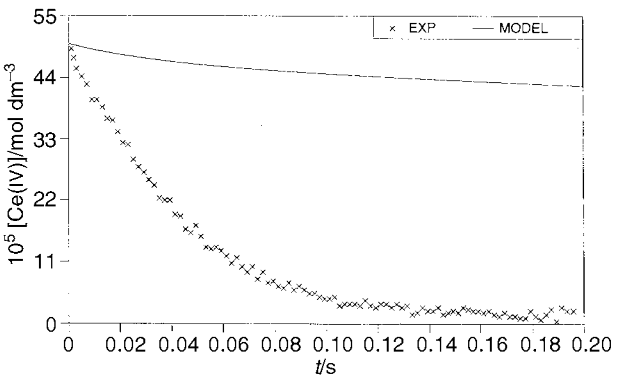

Fig. 2 Reaction of Ce^{IV} with $N_2H_5^+$ + HNO_2 at 25 °C, $10^4[Ce^{IV}] = 5$, $10^3[N_2H_5^+] = 35$, $10^3[HNO_2] = 5$, $[H_2SO_4] = 0.725$ mol dm^{-3}.

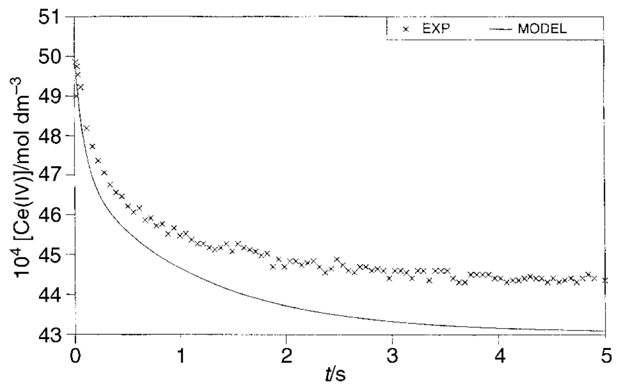

Fig. 3 Reaction of Ce^{IV} with HN_3 + HNO_2 at 25 °C, $10^3[Ce^{IV}] = 5$, $10^4[HN_3] = 2$, $10^4[HNO_2] = 3$, $[H_2SO_4] = 0.725$ mol dm^{-3}. x, Experimental points; full line, computed model.

apparent order of reaction with respect to $[Ce^{IV}]$ can be calculated and was found to be 0.88 for $[N_2H_5^+]_0 = 0.035$ decreasing to 0.81 for $[N_2H_5^+]_0 = 0.0075$ mol dm^{-3}. When $[HNO_2]_0$ was varied it was found that $-(d[Ce^{IV}]/dt)_0$ was proportional to $[HNO_2]_0$.

Kinetics of the $Ce^{IV}/HNO_2/HN_3$ systems

The cerium(IV) consumption experiments that led to the present work involved relatively high concentrations of reagents, *e.g.* $[Ce^{IV}]$ 0.125, $[NaNO_2]$ 0.025 and $[NaN_3]$ 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}/HN_3 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 rates[10] 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 $Ce^{IV}/HNO_2/NH_3OH^+$ and the $Ce^{IV}/HNO_2/NH_2SO_3H$ systems

These experiments were unsuccessful because the reaction of hydroxylamine with nitrous acid is relatively slow[11] and we were unable to obtain any evidence for reaction of Ce^{IV} with any of the postulated intermediates in the HNO_2/NH_3OH^+ 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 NH_2SO_3H. However, in the three reactant system there was no consumption of Ce^{IV}; either the expected intermediates $ON{\cdot}NHSO_3H$ or $HON{=}NSO_3H$ were resistant to oxidation or they decomposed too rapidly.

Stoichiometric experiments on the $Ce^{IV}/HNO_2/HN_3$ system

Most of this work consisted of determining the residual $[Ce^{IV}]$ when a mixture of $NaNO_2$ + NaN_3 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

$$R = ([Ce^{IV}]_0 - [Ce^{IV}]_\infty)/(2[NO_2^-]_0 + [N_3^-]_0) \qquad (9)$$

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 N_2, N_2O and NO_3^-; 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 Sheeres[5] 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 $[H_2SO_4]_{total}$ 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 $red^{+\bullet} + H^+ + e \longrightarrow Hred^+$ make $N_2H_5^+$ and NH_3OH^+ 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 constant[3] 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!

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
$[NO_3^-]_\infty$/mol dm^{-3}	0.034	0.044	0.0286	0.0217

The alternative interpretation is that the conjugate base species NO_2^-, N_3^-, NH_2OH and N_2H_4 react with the oxidant. Writing this in the simplest form of a second order process with (11) as the rate-determining step, and leaving aside the question

$$Hred^+ \xrightleftharpoons{K_a} red + H^+ \quad \text{fast} \qquad (10)$$

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

$$Ce^{IV} + red \xrightarrow{k_8} Ce^{III} + red^{+\bullet} \quad \text{slow} \qquad (11)$$

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

The steps by which $red^{+\bullet}$ radical species such as $N_2H_4^{+\bullet}$, $NH_2OH^{+\bullet}$ 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} $NaClO_4$. This gives the two strongest reducing agents the largest k_8 values with N_2H_4 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 $[Ce(SO_4)_3]^{2-}$, 8% as $Ce(SO_4)_2$, and 0.07% as $[Ce(SO_4)]^{2+}$ with very small amounts of $[Ce(OH)]^{3+}$, Ce^{4+} and $[Ce_2(OH)_2]^{6+}$. 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 reported[19] to be almost constant from 0.5 to 4 mol dm^{-3} sulfuric acid. The value of k_8 for N_2H_4 is only a factor of ten below the encounter limit, and as we calculate *ca.* 8% of the cerium is present as $Ce(SO_4)_2$ this would be consistent with a diffusion controlled reaction between $Ce(SO_4)_2$ and N_2H_4. Presumably, the less sulfated complexes would also react at every encounter. Mishra and Gupta[20] also suggested $Ce(SO_4)_2$ as the active species. However, we are sceptical that such calculations are accurate enough to exclude some contribution from $[Ce(SO_4)_3]^{2-}$, and would merely claim that most of the cerium(IV) complexes react with N_2H_4 at close to the encounter rate.

The same problem arises with the other reductants. Waters and Wilson[4] examined the oxidation of hydroxylamine in 3–9 mol dm^{-3} sulfuric acid and suggested an inner-sphere mechanism involving $Ce(SO_4)_2\cdot NH_2OH$, while Treindl and Viludevá[14] working in 0.5–5 mol dm^{-3} sulfuric acid suggested $[Ce(SO_4)\cdot NH_2OH]^{2+}$. 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 NH_2OH and N_3^- are very similar, *ca.* 10^8 $dm^3\ mol^{-1}\ s^{-1}$, and are significantly below the encounter limit. Hydroxylamine is a much stronger reducing agent, $(E°)_{red}$ for $red^{+\bullet} + e \longrightarrow red$ being 0.42 V[21] compared to 1.33 V for azide,[22] but this may be offset by a much lower self-exchange constant[23] ($\log k_{11} = -12.3$ 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 NO_2–NO_2^- couple[22] 1.04 V, is lower than for the Ce^{IV}–Ce^{III} couple of 1.45 V, so

Table 4 Redox data on nitrogen substrates

$Hred^+$	n	$k_n/dm^3\ mol^{-1}\ s^{-1}$	pK_a	$k_8/dm^3\ mol^{-1}\ s^{-1}$	$(E°)_{red}$/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_3OH^+	4	111	6.06[d]	1.2×10^8	0.42[e]	0.77
$N_2H_5^+$	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.

the oxidation of NO_2^- to NO_2 is reasonable. For the NO_2^+–NO_2 couple[22] $E°$ 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 Ce^{IV}/HNO_2 reaction. They proposed the mechanism in eqns. (13)–(16). We see no reason to

$$Ce^{IV} + NO_2^- \rightleftharpoons [Ce^{IV}\cdot NO_2^-] \quad \text{fast} \qquad (13)$$

$$[Ce^{IV}\cdot NO_2^-] \longrightarrow Ce^{III} + NO_2 \quad \text{slow} \qquad (14)$$

$$2NO_2 \rightleftharpoons N_2O_4 \quad \text{fast} \qquad (15)$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + H^+ + NO_3^- \qquad (16)$$

modify this. The rate data of Swarski *et al.* when interpolated at $[H_2SO_4] = 0.725$ mol dm^{-3} gave $k_2 = 331$ dm^3 mol^{-1} 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 mechansim. Using the simpler form of the Marcus equation[25] without work terms one can use $(E°)_{red}$[22] and the self-exchange constants[23] for red/red$^{+\bullet}$ combined with the k_8 values for total Ce^{IV} to calculate apparent 'self exchange constants' for Ce^{IV}/Ce^{III} in 0.725 mol dm^{-3} sulfuric acid. Such calculations showed no sort of self-consistency, giving values/dm^3 mol^{-1} 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 value[26] of 4.2 dm^3 mol^{-1} s^{-1} for Ce^{IV}/Ce^{III} in 0.4 mol dm^{-3} sulfuric acid at 0 °C. We conclude that these oxidations proceed by an inner sphere mechanism.

The $Ce^{IV}/HNO_2/N_2H_5^+$ 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 $[N_2H_5^+]_0 = 0.035$, $[HNO_2]_0 = 0.0025$, $[Ce^{IV}]_0 = 0.0005$ mol dm^{-3} successive half-lives for Ce^{IV} are 0.0318, 00282, 0.027 s which compare with calculated values for $N_2H_5^+/HNO_2$ 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 study[10] in perchloric acid, assuming that the rate in sulfuric acid would be the same at a given H_o value. The results show that Ce^{IV} reacts rapidly with an intermediate in the hydrazine/nitrous acid reaction, $NH_2N{=}NOH$. 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 $NH_2N{=}NOH$ 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

$$-d[Ce^{IV}]/dt = k_9[Ce^{IV}][NH_2N{=}NOH] \qquad (17)$$

by setting up a series of differential equations for $d[Ce^{IV}]/dt$, $d[N_2H_5^+]/dt$, $d[HNO_2]/dt$ and $d[NH_2N{=}NOH]/dt$ and integrating by the Gear method. A series of values for k_9 was tried and the best fit, shown in the figure, gave $k_9 \approx 10^4$ dm^3 mol^{-1} 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 coworkers[27] of the cerium(IV) reaction with hyponitrous acid $H_2N_2O_2$. Gupta suggested oxidation of HON=NOH to HON=NO$^\bullet$ followed by a further oxidation to the acid form of Angeli's salt, $H_2N_2O_3$ (HON(O)=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 $NH_2N(O){=}NOH$ which could yield NH_2NO + NOH which would give $N_2 + 0.5N_2O + 1.5H_2O$. We have no evidence on this point.

The $Ce^{IV}/HNO_2/HN_3$ 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 NNN–NO_2 or NNN–O–N=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 Czapski[28] to be $>10^6[N_3NO]$ mol dm^{-3} s^{-1}, so an encounter controlled reaction with 0.125 mol dm^{-3} Ce^{IV} could possibly trap N_3NO before it decomposed to $N_2 + N_2O$. 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 $NaNO_2$ + NaN_3 the calculated rates of reactions (5), (3) and (1) are 276, 48 and 0.7 mol dm^{-3} s^{-1} respectively.

The molecule nitryl azide, NNN–NO_2, has been made[29] 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

$$NNN{-}NO_2 \longrightarrow 2N_2O \qquad (18)$$

formed by radical combination it is unlikely to be responsible for the consumption of Ce^{IV}. The isomeric species NNN–O–N=O could also be formed by radical combination, and has been postulated as an intermediate[30] to account for the products of the oxidation of hydrazoic acid by concentrated nitric acid. A fragmentation reaction such as (19) would produce

$$NNN{-}O{-}N{=}O \longrightarrow N_2 + 2NO \qquad (19)$$

nitric oxide which should be readily oxidisable to NO^+ which would hydrate to $HNO_2 + H^+$. 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 dm^3 mol^{-1} 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 timescale. 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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