

Flash Generation and Decay Kinetics of the Nitrate Radical in Aqueous Nitric Acid Solutions¹

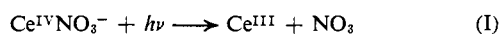
R. W. Glass and T. W. Martin²

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203. Received September 26, 1969

Abstract: The generation and decay kinetics of the NO₃ radical produced at 25 ± 1° by the flash photolysis of ceric ammonium nitrate in aqueous nitric acid solutions ranging from 1 to 15 M are explained fully by the following steps: (I) Ce^{IV}NO₃⁻ + hν → Ce^{III} + NO₃; (II) Ce^{III} + NO₃ → Ce^{IV}NO₃⁻, k_{II}; (III) NO₃ + NO₃ → N₂O₆, k_{III}; (IV) N₂O₆ + 2Ce^{IV} → 2NO₂⁺ + O₂ + 2Ce^{III}; and (V) NO₂⁺ + NO₃⁻ + H₂O ⇌ 2HONO₂. Contrary to other workers, we argue that NO₃ decays only by second-order and not by first-order processes and that (I) is the only necessary and sufficient primary process to generate NO₃ under these conditions. In addition, we can show that steps III and IV are necessary to explain the production of O₂ and the small amount of irreversible bleaching of Ce^{IV} upon photolysis. Although k_{II} is sensitive to HONO₂ activity, k_{III} is constant with a value at 25° of (0.79 ± 0.04) × 10⁶ M⁻¹ sec⁻¹. Finally, the new value for the molar extinction coefficient of NO₃ in these solutions at 6350 Å and 25° (ε_{NO₃,6350}) is 250 ± 90 M⁻¹ cm⁻¹.

A number of investigations concerning the generation and decay of the NO₃ free radical in aqueous solutions have been reported in the literature.³⁻¹⁰

Using a flash photolysis technique, Martin, *et al.*,^{3,4} first showed that NO₃ could be generated efficiently at room temperature in 6.0 M nitric acid (HONO₂) solutions of ceric ammonium nitrate, (NH₄)₂Ce(NO₃)₆. They postulated the primary photochemical process in a generalized notation to be

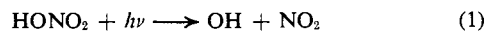


and showed the major pathway for NO₃ disappearance to be the bimolecular process



In 6.0 M HONO₂ solutions they reported k_{II} = (1.70 ± 0.04) × 10⁶ M⁻¹ sec⁻¹ at 23° with an activation energy ≈ 1.0 ± 0.2 kcal/mol. They also noted the permanent photoreduction of a small fraction of the initial [Ce^{IV}].

Hayon and Saito⁵ later suggested that the NO₃ radical was not formed by the direct photolysis of the Ce^{IV} ion, but rather by the direct photolysis of the undissociated HONO₂ solvent molecules in sequence 1-2, whence they presumed the OH radical was precursor to NO₃ in this system. These conclusions were



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(2) To whom correspondence about this paper should be sent. Experimental details can be found in R. W. Glass, Ph.D. Thesis, Vanderbilt University, 1968.

(3) T. W. Martin, A. Henshall, and R. C. Gross, *J. Amer. Chem. Soc.*, **85**, 113 (1963).

(4) T. W. Martin, R. E. Rummel, and R. C. Gross, *ibid.*, **86**, 2595 (1964).

(5) E. Hayon and E. Saito, *J. Chem. Phys.*, **43**, 4314 (1965).

(6) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 3802 (1967).

(7) M. Daniels, *ibid.*, **70**, 3022 (1966).

(8) M. Daniels, *ibid.*, **73**, 3710 (1969).

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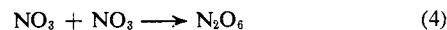
(10) T. W. Martin and R. W. Glass, *J. Amer. Chem. Soc.*, **92**, 5075 (1970).

drawn from their esr study of NO₃ produced upon uv photolysis of aqueous HONO₂ and K₂Ce(NO₃)₆ ices at 77°K and from an earlier study by Husain and Norrish,¹¹ who used sequence 1-2 to explain the production of NO₃ in the flash photolysis of HONO₂ vapor. More recently Dogliotti and Hayon⁶ studied the decay kinetics of NO₃ by using a flash photolysis technique to generate the radical from neat aqueous and HONO₂ solutions of K₂Ce(NO₃)₆ at room temperature. In this work they agreed with Martin, *et al.*,⁴ that the Ce^{IV} species was more intimately involved in explaining the generation of NO₃. However, they maintained that primary process 3 followed by reaction 2 was



necessary to produce NO₃. They further reported the decay of NO₃ to be first order, with a rate constant of 0.95 × 10³ sec⁻¹. This work differs substantially with observations by Martin, *et al.*,⁴ on the same system not only with regard to the primary process and the kinetic order and data analysis of the NO₃ decay process but also in their contention that NO₃ does not react with those Ce^{III} species generated from primary process 3 but does react with the excess Ce^{III} added prior to the flash.

Daniels⁷ later reported the production of NO₃ upon pulse electron radiolysis of concentrated NaONO₂ solutions. In a more recent study⁸ the reaction kinetics of NO₃ in 0.5-6 M NaONO₂ solutions and 6 × 10⁻²-9 M HONO₂ were also considered. He found that NO₃ decayed by first-order kinetics in solutions having pH 4-11, by mixed-order kinetics in neutral solutions, and by second-order kinetics in acid solutions. Although no mechanism was offered for the first-order process, Daniels suggested the second-order decay may result from the reaction



which we first reported on elsewhere.¹ Earlier pulse electron radiolysis of 10⁻³-4.0 M HONO₂ solutions by Broszkiewicz⁹ had produced NO₃ reported to decay by

(11) D. Husain and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **273**, 165 (1963).

the first-order process



with a rate constant of $7.59 \times 10^3 \text{ sec}^{-1}$.

Since we were the first laboratory to discover how to produce and study the NO_3 radical in solution, these obvious inconsistencies in the literature cast serious doubt on some of our initial work. Hence, we set out about three years ago to resolve all we could about questions concerning the generation and decay kinetics of the NO_3 radical produced from Ce^{IV} nitrate salts in aqueous HONO_2 solutions. This effort has resulted in series of papers. The first¹² resulted in reinterpreting some of Hayon and Saito's esr results,⁵ it also proved it is very easy to generate NO_3 without complication from reaction sequence 1-2. The second¹⁰ aims at those questions dealing with process II and the gross structure and identification of all Ce^{III} and Ce^{IV} nitrate species involved in nitric and perchloric acid systems with $[\text{H}^+] \geq 1 \text{ M}$. This third paper contains most of our new work on the detailed kinetics and mechanism of the NO_3 decay processes. It also proves that reaction I is a valid primary process and why, with Ce^{IV} nitrates present, only primary process I is necessary to explain the generation of NO_3 when $[\text{HONO}_2] \geq 1 \text{ M}$. We are preparing a fourth paper in which we hope to show how to choose conditions to select and differentiate between primary processes I and 3.¹³

Experimental Section

1. Chemicals and Sample Solutions. The source and preparation of reagents and solutions are described in detail elsewhere.^{2,10}

Anhydrous HONO_2 was prepared by vacuum distillation of a mixture of NaONO_2 , H_2SO_4 , and 30% fuming H_2SO_4 . Any excess SO_3 was pumped out of the mixture and discarded. The anhydrous acid was kept frozen at -195° and stored in the dark until used, at which time it was allowed to warm to $25 \pm 1^\circ$. The density of the acid was found to be $1.512 \pm 0.010 \text{ g/cc}$ (25°) which, within experimental uncertainty, agrees with the literature value of 1.504 g/cc (25°).¹⁴ Hence, if water is present, its level of concentration may be estimated as $<0.1\%$ or $<0.12 \text{ M}$. All stock solutions were prepared under helium purge.

2. Spectrophotometric Techniques. To study the permanent bleaching of $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$ a special technique was developed in which a sample could be exposed to a single or successive flashes of the photolysis lamp, then analyzed for any permanent change in the $[\text{Ce}^{\text{IV}}]$. Using the fixed geometry of the sample cell in the photolysis lamp and discharging the lamp under identical conditions (40 Torr oxygen pressure with $1.0 \mu\text{F}$ at 15-kV discharge energy) the total number of quanta available to the sample per flash was maintained essentially constant. By carefully adjusting the $[\text{Ce}^{\text{IV}}]$ in any given set of runs, so as to match the initial Ce^{IV} absorption curves, a relatively constant number of quanta absorbed by each solution was ensured. The change in $[\text{Ce}^{\text{IV}}]$ per flash was determined spectrophotometrically upon comparison with an unphotolyzed and known solution of Ce^{IV} . Each bleaching run was conducted several times on fresh aliquots and the average absorbance change determined.

For bleaching runs at 0.5 and 75° (see Table V) the quartz photolysis cell containing the Ce^{IV} sample was allowed to equilibrate thermally in the dark to the desired temperature in a water bath prior to flashing. The sample cell was then rapidly transferred to the photolysis lamp and flashed.

3. Micromolar Gas Handling Techniques. Two techniques which involved handling micromolar quantities of gases provided important clues in establishing the mechanism for NO_3 decay.

In the first analysis, exactly 4.00 ml of $3.99 \times 10^{-3} \text{ M Ce}^{\text{IV}}$ in 2.00 M HONO_2 was pipetted into a special Pyrex photolysis cell of the same dimensions as the usual quartz cell.^{2,4} The Pyrex cell was connected by its side arm to a Thunberg tube designed to fit a high-vacuum line for degassing the sample. The aliquot of Ce^{IV} stock solution was flushed with dry helium for 5 min, then placed on a vacuum line at 10^{-5} Torr for degassing. A series of four freeze-pump-thaw cycles was sufficient. The degassed sample was kept under vacuum, removed from the vacuum line, and allowed to come to temperature equilibrium at 25° . Then the solution was carefully transferred within the special cell from the Thunberg tube to the photolysis cell section and flashed 20 times, care being taken to remove the cell to agitate the solution between each flash. Following photolysis, the cell was returned to the vacuum line and the solvent was slowly distilled into a Dry Ice-acetone trap followed by a liquid nitrogen trap. Any noncondensable gas present was transferred *in vacuo* to a gas buret for volume measurement and then to a gas chromatograph for identification. The Ce^{IV} salt remaining in the Thunberg tube was carefully redissolved in exactly 4.00 ml of 2.00 M HONO_2 stock. An aliquot of this solution was placed in a dry Cary 14 sample cell and the absorption curve was recorded. By comparing this curve with one recorded on the Ce^{IV} solution prior to photolysis, the change in $[\text{Ce}^{\text{IV}}]$ was determined. A blank run was made using a 4.00-ml aliquot of 2.00 M HONO_2 without Ce^{IV} to prove that the noncondensable gas did not arise from direct photolysis of the HONO_2 solvent.

In the second analysis, a cold-finger trap of predetermined volume (9.3 cc) was placed on the vacuum line and filled to a pressure of 14.9 Torr with NO_2 . The stopcock on the trap was closed and the NO_2 frozen out at -195° . Exactly 4.00 ml of $5.05 \times 10^{-3} \text{ M Ce}^{\text{IV}}$ in 2.00 M HONO_2 solution was delivered to a Thunberg tube placed on the vacuum line at 10^{-5} Torr and thoroughly degassed. The trap containing the NO_2 was placed at a common inlet position on the vacuum line so that, by distillation, the NO_2 could be transferred *in vacuo* to the Thunberg tube containing the Ce^{IV} solution. Upon thawing and gently agitating the solution, the NO_2 immediately reduced a fraction of the Ce^{IV} to Ce^{III} . An aliquot of the reduced Ce^{IV} solution was placed in a dry Cary 14 sample cell and the absorption curve recorded. By comparing this curve with one recorded prior to the Ce^{IV} reduction by NO_2 , the change in $[\text{Ce}^{\text{IV}}]$ was determined.

4. Optical, Electronic, and Photographic Techniques. The flash spectroscopic and kinetic techniques used were essentially the same as those described previously.^{2-4,10}

One improvement in the flash kinetic detection system was the substitution of a more sensitive RCA Type 7265 photomultiplier for the RCA Type 1P28 previously used.⁴ This 14-stage, end-window tube having an S-20 response was coupled directly to the exit optics from the Bausch and Lomb 250-mm grating monochromator (dispersion = 66 \AA/mm). The increased sensitivity of this photomultiplier allowed entrance and exit slits of the monochromator to be closed down to 0.5 mm each to monitor a narrower 32- \AA wavelength band at $6350 \pm 16 \text{ \AA}$ as compared to the 160- \AA band monitored earlier.¹⁰ The output from the 7265 was coupled to the oscilloscope by a 6BQ7A cathode follower to prevent cable attenuation of the signal.

5. Data Processing. The experimental procedures and computer techniques used for analyzing NO_3 decay data recorded on 35-mm film strips are described in detail elsewhere.^{2,10}

Results and Discussion

1. The Primary Photochemical Process. With the present apparatus the transient decay can be observed over a period from 65 to 2000 μsec after the photolysis flash is triggered with a maximum uncertainty in time measurement of $\pm 1 \mu\text{sec}$. After triggering, the photolysis flash rises to a maximum output intensity in 10 μsec and decays to within 1% of zero intensity in $\approx 65 \mu\text{sec}$. Within the limits of our criteria for data collection,^{2,10} the first reliable data on the NO_3 absorption are recorded at a time $\geq 55 \mu\text{sec}$ following the peak flash intensity. By an extrapolation technique, we use this initial "blind" period of about 55 μsec , while the primary photochemical process is being completed, to check on the internal consistency of our best flash data. However, before discussing that, the importance of

(12) T. W. Martin, L. L. Swift, and J. H. Venable, Jr., *J. Chem. Phys.*, **52**, 2138 (1970).

(13) T. W. Martin and L. L. Swift, unfinished work.

(14) W. Davis, Jr. and H. J. DeBruin, *J. Inorg. Nucl. Chem.*, **26**, 1069 (1964).

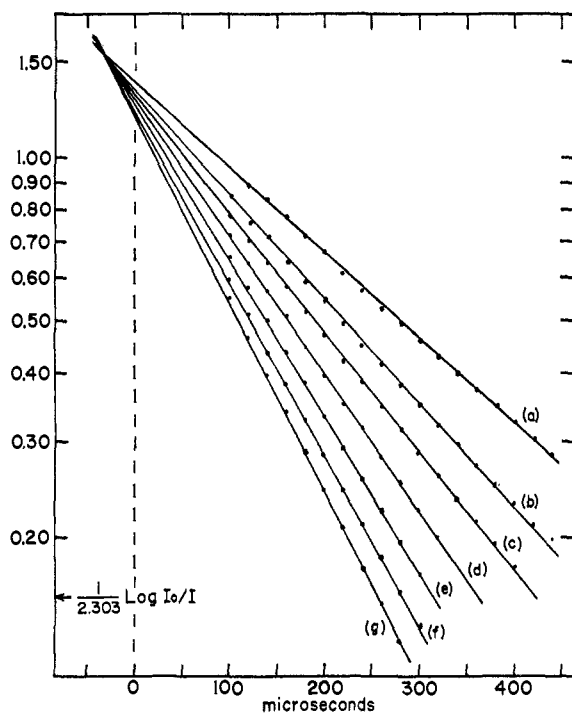


Figure 1. Plots of average pseudo-first-order NO_3 decay data in 2.00 M HONO_2 at $25 \pm 1^\circ$ (see Table I). $[\text{Ce}^{\text{III}}]_{\text{A}} \times 10^3\text{ M}$: (a) 3.95, (b) 4.88, (c) 6.02, (d) 6.92, (e) 8.02, (f) 9.19, and (g) 10.35.

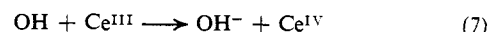
careful solvent blank runs should be mentioned. In the previous paper,¹⁰ the region of maximum NO_3 absorption at $6350 \pm 80\text{ \AA}$ was monitored while each of 17 stock solutions from 1.0 to 15.0 M HONO_2 was flash photolyzed in the absence of Ce^{IV} . Although the technique was capable of detecting very small changes in absorbance (≈ 0.01), there was no change in the 100% transmission. Hence, it was concluded that the quantity of NO_3 arising through direct photolysis of HONO_2 molecules by process 1 was either negligible or nonexistent in these solutions at 25° . However, similarly photolyzed samples of the same HONO_2 solutions with Ce^{IV} ions present revealed NO_3 generation in every case with yields big enough to identify the radical by its three characteristic absorption band maxima at 5980, 6350, and 6710 \AA . These data prove that the Ce^{IV} species must be directly involved in the generation of the NO_3 radical.

In order to further understand the role of Ce^{IV} in NO_3 production, it is useful to consider the earlier results of Martin, *et al.*⁴ Using $1.01 \times 10^{-3}\text{ M Ce}^{\text{IV}}$ in 6.0 M HONO_2 , they found that adding increasing quantities of Ce^{III} to the solution prior to the flash simplified the second-order decay kinetics of NO_3 to the form

$$-d[\text{NO}_3]/dt = k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{E}}[\text{NO}_3] = k'[\text{NO}_3] \quad (6)$$

Here, $k' = k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{E}}$ is the pseudo-first-order rate constant derived from the decay data and $[\text{Ce}^{\text{III}}]_{\text{E}}$ is the effective $[\text{Ce}^{\text{III}}]$ at "zero" time ($t = 0$) for the reaction. Actually $[\text{Ce}^{\text{III}}]_{\text{E}}$ is the sum of two terms: the quantity of Ce^{III} added to the solution prior to the flash, $[\text{Ce}^{\text{III}}]_{\text{A}}$, and the quantity of Ce^{III} generated during the flash, $[\text{Ce}^{\text{III}}]_{\text{G}}$. Under identical photolysis conditions, pseudo-first-order decay data for five different increasing values of $[\text{Ce}^{\text{III}}]_{\text{A}}$ gave linear plots

which, when extrapolated backward in time, were found to intersect at a common point corresponding to the peak flash intensity. Since the value of $[\text{NO}_3]_{t=0}$ is unchanged by changing $[\text{Ce}^{\text{III}}]_{\text{A}}$, they concluded that $[\text{NO}_3]_{t=0} = [\text{Ce}^{\text{III}}]_{\text{G}}$. In contrast, with $[\text{HONO}_2] < 3.0\text{ M}$, Dogliotti and Hayon⁶ reported a decrease in $[\text{NO}_3]_{t=0}$ with increasing values of $[\text{Ce}^{\text{III}}]_{\text{A}}$. These workers postulated that through process 7 the added



Ce^{III} acted as a scavenger for the OH radicals produced in primary process 3. In their view, the competition between reactions 7 and 2 could explain the initial radical concentration dependence on $[\text{Ce}^{\text{III}}]_{\text{A}}$. Unfortunately, their interpretation ignores the magnitude of the $[\text{Ce}^{\text{III}}]_{\text{G}}$ term and the ability of this material to also react with NO_3 just as the $[\text{Ce}^{\text{III}}]_{\text{A}}$ reacts.

To critically test the validity of our $[\text{Ce}^{\text{III}}]_{\text{G}}$ term, sets of pseudo-first-order runs were conducted in 2.00 M HONO_2 solutions. This value for $[\text{HONO}_2]$ was selected purposely to test Dogliotti and Hayon's results as well as to safely avoid possible ambiguities in interpretation of the primary process due to the presence of nonnitrated hydrolysis products of Ce^{IV} , which are possible when $[\text{HONO}_2] < 1\text{ M}$. Upon integrating and rewriting in terms of absorbance,¹⁰ eq 6 becomes

$$\ln [\log \bar{I}_0/I]_t = -k't + \ln [\log \bar{I}_0/I]_{t=0} \quad (8)$$

Least-squares best fits of our NO_3 decay data are plotted in Figure 1 using the values of $[\log \bar{I}_0/I]_{t=0}$ and k' in Table I. Each decay curve displays averaged NO_3 decay data from at least six kinetic runs, each run made on fresh aliquots of the same solution. It is obvious that all of the decay curves are extrapolated to a common point in time which we find coincident with the peak of the photolysis flash intensity. Furthermore, the values of $[\log \bar{I}_0/I]_{t=0}$ are not found to decrease as $[\text{Ce}^{\text{III}}]_{\text{A}}$ increases, but instead better define the experimental deviation about a mean value of $[\log \bar{I}_0/I]_{t=0} = 1.61 \pm 0.10$. Unfortunately, Dogliotti and Hayon provided only bare plots with no estimates of experimental precision, making it impossible to examine the validity of their argument in favor of primary process 3. However, there are many experimental uncertainties in evaluating flash data and, consequently, there is uncertainty in any extrapolation technique to obtain an intercept value which corresponds to $[\text{NO}_3]_{t=0}$. This is particularly true when it is realized that Dogliotti and Hayon attempted to use absorbance values two orders of magnitude smaller than used in the present work. Hence, we conclude that their arguments and evidence in favor of a physically unobserved OH radical precursor to NO_3 are not sufficient. Furthermore, it is not possible by an analysis of NO_3 decay data alone, no matter how precise, to discriminate between primary processes 1 and 3. So let us consider some other ways to attack this problem.

Any attempt which hopes to resolve these two logical paths for electron transfer must be based ultimately on an understanding of the complex character of Ce^{IV} in solution. In dilute aqueous solutions Ce^{IV} exists as a highly aquated species, in which the number of water molecules associated with the first coordination layer is unknown. As a consequence, in solutions of

Table I. Summary of Pseudo-First-Order Data in 2.00 M HONO₂ at 25 ± 1°

Curve ^a	Initial sample composition			Observed rate data		
	[Ce ^{IV}] × 10 ³ M	[Ce ^{III}] _A × 10 ³ M	Log I ₀ /I at t = 0	Half-life, μsec	k' × 10 ⁻³ sec ⁻¹	k _{II} ^b × 10 ⁻⁶ M ⁻¹ sec ⁻¹
a	1.00	3.95	1.55	195	3.53	0.745
b	1.01	4.88	1.46	167	4.21	0.747
c	1.00	6.02	1.56	141	4.98	0.731
d	1.00	6.92	1.64	118	5.90	0.761
e	1.01	8.02	1.70	102	6.78	0.762
f	1.01	9.19	1.67	95	7.39	0.737
g	1.00	10.35	1.72	86	8.13	0.723
			Av 1.61 ± 0.10			Av 0.744 ± 0.015

^a Alphabetical labels correspond to the data plots in Figure 1. ^b Calculated assuming $\epsilon_{\text{NO}_3}^{6360} = 1.92 \times 10^3 \text{ M}^{-1}$.

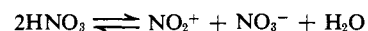
low acid concentration, Ce^{IV} tends to form highly hydrolyzed and polymerized species¹⁵ (e.g., Ce(OH)³⁺, Ce(OH)₂²⁺, (CeOCE)⁶⁺, (CeOCEOH)⁵⁺, etc). Because hydrolysis effects are so uncertain and are often irreversible, it is standard procedure in our laboratory always to add the dry Ce^{IV} salt to a solvent containing HONO₂ or HOClO₃ ≥ 1 M.

In HONO₂ solutions, both spectrophotometric¹⁶ and electrophoresis¹⁷ studies confirm that nitrate complexation occurs with the Ce^{IV} cation. It would appear that anionic complexes, as Ce(H₂O)_n(NO₃)₅⁻ and Ce(H₂O)_n(NO₃)₆²⁻, exist in solutions where [HONO₂] > 5.0 M, but that interaction between nitrate ions and the hydrated Ce^{IV} species decreases rapidly at lower [HONO₂], eventually yielding some nonnitrated hydrolysis products for [HONO₂] < 1.0 M. Since Dogliotti and Hayon⁶ first postulated primary process 3 to be operative in solutions where [HONO₂] ≤ 1.0 M and then extended its applicability to solutions where 1.0 M ≤ [HONO₂] ≤ 6.0 M, it seemed crucial for us to prove whether or not H₂O was necessary for the production of NO₃. We thus set out to find if the NO₃ free radical could be generated in anhydrous HONO₂. If so, it would prove unequivocally that reaction sequence 3-2 was not necessary to explain NO₃ generation under our conditions, but that primary process I was. Anhydrous HONO₂ was selected as the solvent because it dissolves sufficient quantities of the Ce^{IV} salt for flash work, it can be prepared using common vacuum distillation techniques, and it does not react with NO₃ to preclude spectroscopic identification of the radical.

A 6.3 × 10⁻⁴ M Ce^{IV} sample in anhydrous HONO₂ was placed in the predried photolysis cell and capped tightly. Using our flash spectroscopic technique, four runs were conducted on different aliquots of this solution with selected spectroscopic flash delays of 10, 15, 30, and 40 μsec, respectively, after the initiation of the photolysis flash. The NO₃ absorption spectrum was observed in each run, accompanied by an apparent permanent bleaching of the Ce^{IV} absorption. Flash photolyzed samples of the anhydrous acid without added Ce^{IV} showed no evidence of NO₃.

Although density measurements indicated that the anhydrous acid was 100 ± 0.1% HONO₂, it is impossible to preclude the presence of a trace of water as an impurity. However, considering the strong inter-

action of H₂O with this solvent and the unfavorable entropy factors involved for a trace of H₂O to localize only on the Ce^{IV} ions, we argue that a trace of H₂O cannot compete with the bulk HONO₂ for sites in the coordination sphere of Ce^{IV}. Our argument is bolstered by other facts. For example, it is well known that pure HONO₂ undergoes considerable "self-ionization." This process may be summarized as



where the water molecule produced exists as a solvated molecular species. Ingold and coworkers¹⁸ have shown that even in HONO₂ solutions containing up to 5% H₂O by weight, the water molecules are fully solvated by the acid, e.g., H₂O·(HONO₂)₂. A discussion of the solvation of water by HONO₂ and of the other physical properties of the anhydrous acid can be found in an exhaustive review by Stern, Mullhaupt, and Kay.¹⁹ It is of further interest that recent X-ray diffraction²⁰ and infrared and Raman²¹ studies have indicated that even in saturated aqueous solutions of (NH₄)₂Ce(NO₃)₆, nitrate ligands predominate over hydration in the first coordination sphere of Ce^{IV}.

Thus, there is absolutely no question that in the anhydrous limit reaction I is the one and only primary process. Conversely, in the limit where there is no NO₃⁻ present, in strong acids such as H₂SO₄, H₃PO₄, and HOClO₃, Moorthy and Weiss²² have undoubtedly proved that primary process 3 reigns supreme. In a forthcoming paper¹³ we hope to show how one can choose conditions to observe and to change the balance between these two competitive primary processes. However, we are convinced from our experience¹⁰ that reaction I is the overwhelmingly predominant photochemical process operative in aqueous HONO₂ solutions ranging from about 1 M to the anhydrous limit.

2. The Kinetic Order of the NO₃ Decay Process. Martin, *et al.*,⁴ working in solutions of 1.01 × 10⁻³ M (NH₄)₂Ce(NO₃)₆ in 6.0 M HONO₂ showed that the average of eight flash kinetic runs yielded a second-order decay curve for NO₃. In contrast, Dogliotti and Hayon⁶ stated that NO₃ decays by a first-order process in solutions of K₂Ce(NO₃)₆ in 2.0, 3.0, and 6.0 M HONO₂.

(18) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *ibid.*, 2559 (1950).

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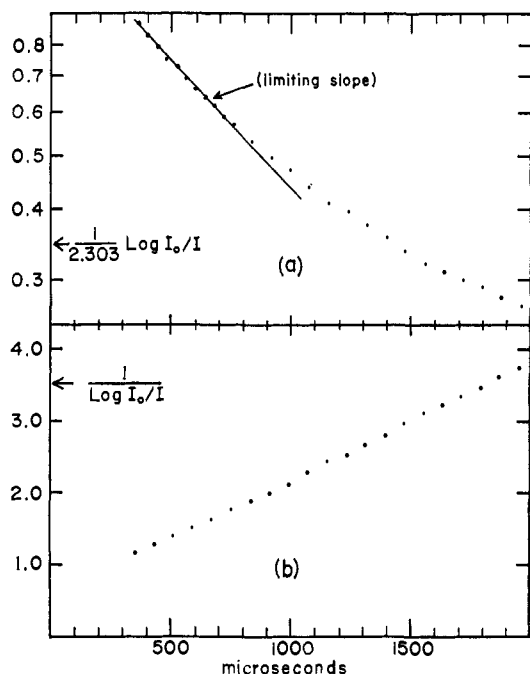


Figure 2. Plots of average NO_3 decay data in 3.50 M HONO_2 at $25 \pm 1^\circ$ in terms of (a) first-order kinetics and (b) second-order kinetics.

We checked these conflicting results with sets of flash kinetic runs on solutions of $1.0 \times 10^{-3}\text{ M (NH}_4)_2\text{-Ce(NO}_3)_6$ in $3.50, 8.00, 13.0,$ and 15.0 M HONO_2 , where no Ce^{III} was added prior to the flash. Each set consisted of six different kinetic runs, and each run was conducted on a fresh aliquot of the sample stock solution. Each set of absorbance data was treated in terms of first-order kinetics using expression 8 and in terms of second-order kinetics based on the symmetrical rate expression

$$-d[\text{NO}_3]/dt = k_9[\text{Ce}^{\text{III}}][\text{NO}_3] = k_9[\text{NO}_3]^2 \quad (9)$$

Upon integrating and rewriting in terms of absorbance, expression 9 becomes

$$1/[\log \bar{I}_0/I]_t = (k_9/\epsilon_{\text{NO}_3} \lambda) t + 1/[\log \bar{I}_0/I]_{t=0} \quad (10)$$

where $\epsilon_{\text{NO}_3} \lambda$ is the molar extinction coefficient of NO_3 at wavelength λ , and l is the optical path length through which the absorbance is measured.

Figure 2 displays a typical example of averaged NO_3 decay data for the set of runs in 3.50 M HONO_2 , being plotted in terms of expressions 8 and 10. Again $t = 0$ on the time coordinate refers to peak flash intensity. In order to display a significant portion of the decay, the oscilloscope was set to sweep for a period of $2000\text{ }\mu\text{sec}$ and owing to the large initial absorbance (≥ 1.0), the first data point was not recorded until $360\text{ }\mu\text{sec}$ after peak flash intensity. In Figure 2a one sees that the first-order plot displays an obvious curvature in the trend of the data points. However, in Figure 2b the second-order plot reveals that the data points fit a good straight line initially but there is a slight deviation from linearity at longer times. (We shall explain that slight deviation later on.) Similar plots of the data from the runs on $8.00, 13.0,$ and 15.0 M HONO_2 give a better fit in terms of second-order kinetics in each case, although we find that the slight deviations

from linearity increase more rapidly with increasing $[\text{HONO}_2]$.

The fact that NO_3 appears to decay in these HONO_2 solutions by a second-order process suggests that a reexamination of the work of Dogliotti and Hayon should be made.⁶ These workers stated that NO_3 decays by a first-order process with a rate constant which was essentially independent of $[\text{HONO}_2]$; however, as shown in Table II, their values for k'

Table II. Summary of First-Order Decay Constants for NO_3 as Reported by Dogliotti, *et al.*,⁶ at $24 \pm 1^\circ$

Initial sample composition [Ce ^{IV}], ^a M	[HONO ₂], M	Observed rate data $k' \pm \sigma \times 10^{-3}\text{ sec}^{-1}$
0.10	0.0 ^b	0.91 ± 0.06
0.10	0.1	0.94 ± 0.02
0.10	2.0	0.97 ± 0.03
0.10	3.0	1.30 ± 0.20
5×10^{-2}	3.0	0.91 ± 0.10
10^{-3}	6.0	0.50 ± 0.10

^a Source of Ce^{IV} was $\text{K}_2\text{Ce(NO}_3)_6$. ^b Unbuffered solution, pH 0.65.

decrease by almost a factor of 2 in going from unbuffered aqueous solutions to 6.0 M HONO_2 . These authors report $k' = 0.95 \times 10^3\text{ sec}^{-1}$, which would imply a reaction half-life of $\approx 730\text{ }\mu\text{sec}$, but their first-order decay curves extend only over a period of about $500\text{ }\mu\text{sec}$. Hence, their decay data represent less than a single half-life for this fast reaction. In contrast, the results from this study indicate that the rate constants given by their data in Table II must represent a limiting slope to our decay curves. To test this idea, the first-order rate constant for our flash kinetic data from the 3.50 M HONO_2 runs was determined employing expression 8. Using only those data points between $t = 0$ and $t = 720\text{ }\mu\text{sec}$, the value of $k' = 1.07 \times 10^3\text{ sec}^{-1}$ was obtained, which is in fair agreement with their reported value. This is the "limiting slope" which is presented in Figure 2a. Similar limiting slope treatment of the data from the $8.00, 13.0,$ and 15.0 M HONO_2 runs yielded the k' values given in Table III. In this table each k' rep-

Table III. Comparison of First- and Second-Order Fits of Flash Kinetic Data in Aqueous HONO_2 Solutions at $25 \pm 1^\circ$ ^a

[HONO ₂], M	$t,^b\text{ }\mu\text{sec}$	$k' \pm \sigma$ $\times 10^{-3}\text{ sec}^{-1}$	Std dev of Absorbance		Reaction order, n
			First- order fit \times 10^3	Second- order fit \times 10^3	
3.50	720	1.07 ± 0.02	5.10	3.78	1.95
3.50	1960	0.71 ± 0.03	29.3	9.54	
8.00	960	1.35 ± 0.02	11.2	4.98	1.80
13.00	480	2.00 ± 0.04	7.56	7.40	1.65
15.00	640	1.69 ± 0.03	12.3	8.20	1.66

^a In every case the initial $[\text{Ce}^{\text{IV}}] = 1.0 \times 10^{-3}\text{ M}$. ^b Reference point, $t = 0$, taken at the peak intensity of the photolysis flash.

resents a least-squares fit of the data only up to the specified reaction time t , with the uncertainties being obtained also by a standard least-squares technique. By considering the data in the 3.5 M HONO_2 runs

through $t = 1960 \mu\text{sec}$, one sees that the standard deviation of absorbance for the first-order fit of the data increases appreciably over that of the second-order fit; however, upon considering only those data for the limiting slope, the standard deviation of absorbance becomes quite similar for fitting the curve by either first- or second-order kinetics. Hence, it becomes obvious that the discrimination between kinetic orders either by graphical means or by comparison of standard deviations of absorbance is less definitive in the limit of sufficiently short reaction times; but in no case are first-order data better.

As a final test of the order for NO_3 decay, the rate expression was written in a general n th-order form as $-\text{d}[\text{NO}_3]/\text{d}t = C[\text{NO}_3]^n$. Hence, a plot of $\log(-\text{d}[\log \bar{I}_0/I]/\text{d}t)$ vs. $\log[\log \bar{I}_0/I]$ for each set of runs gave a straight line whose slope was equal to the reaction order, n . These values for n are given in the last column of Table III. Here one sees that the value of n for the data from the runs in $3.50 M \text{HONO}_2$ is almost 2, but n tends to be <2 with increasing $[\text{HONO}_2]$ for reasons we shall explain later.

We feel that the kinetic data obtained in this work were considered over a sufficient time period to properly evaluate the reaction order and that the absorbance values considered ($\log \bar{I}_0/I = 0.1$ to 0.9) were of an adequate magnitude to eliminate significant reading errors from the oscillograms. In view of the above results, we concluded that NO_3 does not decay by a first-order process in the absence of added Ce^{III} or other reactants, but decays essentially by a second-order process over a wide range of $[\text{HONO}_2]$ as was first claimed.⁴

3. The Reaction of NO_3 with Ce^{III} Formed in the Primary Process. Since NO_3 decays essentially by a second-order process, it is necessary to consider the implications this presents in terms of the decay mechanism. Martin, *et al.*,⁴ assumed that NO_3 must disappear either through a radical dimerization process or by means of the spontaneous reverse electron transfer process (II). The latter route was selected when excess Ce^{III} added prior to the flash reduced the decay order to pseudo-first-order kinetics. However, in keeping with the time resolution capabilities of the flash apparatus, it was not possible to add sufficient $[\text{Ce}^{\text{III}}]_{\text{A}}$ to avoid correction for the $[\text{Ce}^{\text{III}}]_{\text{G}}$ generated by the primary process in $6.0 M \text{HONO}_2$ solutions. For this reason, consistent values for k_{II} were obtained by using the simple rate expression (6) which we now write as

$$-\text{d}[\text{NO}_3]/\text{d}t = k'[\text{NO}_3] = k_{\text{II}}([\text{Ce}^{\text{III}}]_{\text{G}} + [\text{Ce}^{\text{III}}]_{\text{A}})[\text{NO}_3] = k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{E}}[\text{NO}_3] \quad (11)$$

Dogliotti and Hayon⁶ concluded erroneously that NO_3 decays by a first-order process and that NO_3 does not react with $[\text{Ce}^{\text{III}}]_{\text{G}}$. But when excess Ce^{III} was added to the solution prior to the flash, they reported that NO_3 did react with $[\text{Ce}^{\text{III}}]_{\text{A}}$ by the bimolecular process (II). Their pseudo-first-order kinetic scheme may be written as

$$-\text{d}[\text{NO}_3]/\text{d}t = k'[\text{NO}_3] = (k + k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{A}})[\text{NO}_3] \quad (12)$$

Expressions 11 and 12 are mathematically similar but differ in the interpretation of the k and $k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{G}}$ terms. We have already shown in the absence of

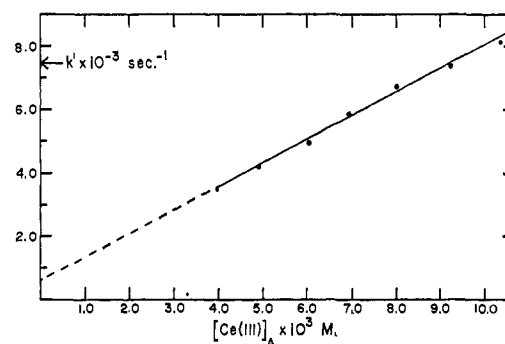


Figure 3. Plot of pseudo-first-order rate constants vs. $[\text{Ce}^{\text{III}}]_{\text{A}}$ in $2.00 M \text{HONO}_2$ (see also Table I).

$[\text{Ce}^{\text{III}}]_{\text{A}}$ that k is not a true first-order rate constant. Further, we are given no evidence⁶ to explain why there should be any difference in reactivity between flash generated Ce^{III} ions and those added prior to the flash. In fact, our second-order kinetic data show convincingly that the NO_3 can see no distinction in these Ce^{III} species. This is exactly what one would anticipate because the necessary rearrangements of associated ligands about each Ce^{III} ion formed in the primary process are sufficiently fast that they are indistinguishable from the excess Ce^{III} species already present by the time the decay data are collected. Hence, we are confident that our $[\text{Ce}^{\text{III}}]_{\text{G}}$ term is a valid correction factor which contributes to the total Ce^{III} population.

In any pseudo-order process the concentration of that reactant which is in considerable excess remains essentially constant during the course of the reaction. The necessity of a valid correction term such as $[\text{Ce}^{\text{III}}]_{\text{G}}$ must mean that each particular value of $[\text{Ce}^{\text{III}}]_{\text{E}}$ is essentially a constant averaged over the entire decay curve. The pseudo-first-order kinetics we observed and the consistent values for k_{II} obtained are solid support for this interpretation. Furthermore, in accord with primary process I, we concluded that $[\text{Ce}^{\text{III}}]_{\text{G}} = [\text{NO}_3]_{t=0}$, from which one may calculate the quantity $\epsilon_{\text{NO}_3}^{6350} = [\log \bar{I}_0/I]_{t=0}/[\text{NO}_3]_{t=0} = (1.92 \pm 0.10) \times 10^3 M^{-1}$, where the values $[\log \bar{I}_0/I]_{t=0} = 0.77$ and $[\text{Ce}^{\text{III}}]_{\text{G}} = (0.40 \pm 0.02) \times 10^{-3} M$ were cited in $6.0 M \text{HONO}_2$ solutions.⁴ Hence, the value $\epsilon_{\text{NO}_3}^{6350}$ may be used to determine $[\text{Ce}^{\text{III}}]_{\text{G}}$ from $[\log \bar{I}_0/I]_{t=0}$ provided l remains constant and the extinction coefficient $\epsilon_{\text{NO}_3}^{6350}$ does not change with $[\text{HONO}_2]$.

In order to test eq 11, the sets of pseudo-first-order data presented in Table I were used. Prior to these runs it was confirmed spectroscopically that the change from 6.0 to $2.00 M \text{HONO}_2$ had no significant effect on the NO_3 absorption spectrum reported earlier.³ So that the present results might be compared with those of Martin, *et al.*,⁴ the same quartz sample cell was used and l remained unchanged. The values for k_{II} given in Table I were determined assuming $\epsilon_{\text{NO}_3}^{6350} = 1.92 \times 10^3 M^{-1}$ to correct for $[\text{Ce}^{\text{III}}]_{\text{G}}$. To check the agreement of the value for $\epsilon_{\text{NO}_3}^{6350}$ from the $2.00 M$ data, the reported values of $[\text{Ce}^{\text{III}}]_{\text{A}}$ were plotted vs. the measured values of k' as shown in Figure 3. In accord with (11) such a plot has a slope which is equal to k_{II} and an intercept which relates the value of $k_0' = k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{G}}$. A least-squares treatment of the data shown in Figure 3 gave $k_{\text{II}} = (0.739 \pm 0.027) \times 10^6$

Table IV. Estimations of the Bimolecular Rate Constant for Process III, $\text{NO}_3 + \text{NO}_3 \xrightarrow{k_{\text{III}}} \text{N}_2\text{O}_6$, in HONO_2 Solutions at $25 \pm 1^\circ$

Figure no. ²	$[\text{HONO}_2],^a M$	$t,^b \mu\text{sec}$	$k_9/\epsilon_{\text{NO}_3}^{6350} l \times 10^{-3} \text{sec}^{-1}$	k_9^c	k_{II}^d $\times 10^{-6} M^{-1} \text{sec}^{-1}$	k_{III}^e
4b	3.50	720	1.48	2.77	1.11	0.83
5b	8.00	960	2.22	4.15	2.55	0.80
5a	13.00	480	3.01	5.63	4.13	0.75
4a	15.00	640	2.73	5.10	3.59	0.76
						Av 0.79 ± 0.04

^a In each solution $[\text{Ce}^{\text{IV}}] = 1.0 \times 10^{-3} M$ initially. ^b Reference point, $t = 0$, taken at the peak intensity of the photolysis flash. ^c Calculated assuming $\epsilon_{\text{NO}_3}^{6350} l = 1.87 \times 10^3 M^{-1}$. ^d Bimolecular rate constants obtained from published pseudo-first-order data.⁹ ^e $k_{\text{III}} = (k_9 - k_{\text{II}})/2$.

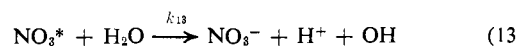
$M^{-1} \text{sec}^{-1}$ and $[\text{Ce}^{\text{III}}]_{\text{G}} = k_0/k_{\text{II}} = (0.86 \pm 0.28) \times 10^{-3} M$. Assuming $[\text{Ce}^{\text{III}}]_{\text{G}} = [\text{NO}_3]_{t=0}$, the average value of $[\log \bar{I}_0/I]_{t=0}$ from Table I may be used to calculate $\epsilon_{\text{NO}_3}^{6350} l = [\log \bar{I}_0/I]_{t=0}/[\text{NO}_3]_{t=0} = (1.87 \pm 0.62) \times 10^3 M^{-1}$ which, within experimental uncertainty, agrees well with the value determined in 6.0 M HONO_2 solutions.⁴ This agreement is further reflected by the value of k_{II} determined in Table I and that obtained from the slope of the curve in Figure 3. It then is safe to assume that $\epsilon_{\text{NO}_3}^{6350}$ remains constant upon changing $[\text{HONO}_2]$. This further test of the $[\text{Ce}^{\text{III}}]_{\text{G}}$ term proves again that NO_3 reacts with those Ce^{III} ions formed during the flash.

It is of interest to compare the value of $\epsilon_{\text{NO}_3}^{6350}$ obtained in this study with that obtained by Schott and Davidson in the gas phase.²³ To determine $\epsilon_{\text{NO}_3}^{6350}$ from the product $\epsilon_{\text{NO}_3}^{6350} l = (1.87 \pm 0.62) \times 10^3 M^{-1}$ one must assess the optical path length, l , through which NO_3 absorbance is measured. Ideally, such a path length should contain a uniform density of absorbing species; however, the flash-photolyzed sample solution presents a gradient of $[\text{NO}_3]$ which decreases radially toward the axis of the cylindrical sample cell. Thus, the absorbance is averaged over an effective path length for which we estimate $l = 7.5 \pm 1$ cm. The upper limit of 8.5 cm is that length subtended by the separation of lamp electrodes between which the flash discharge occurs.⁴ On this basis, $\epsilon_{\text{NO}_3}^{6350}$ is $250 \pm 90 M^{-1} \text{cm}^{-1}$ at 25° . Schott and Davidson estimated in the gas phase that the NO_3 bands at 6340 and 6620 Å have a maximum value at 25° of $3000 \pm 1000 M^{-1} \text{cm}^{-1}$. This estimate was made from their photographic records of NO_3 in a shock pyrolysis study at $\approx 825^\circ\text{K}$. This order of magnitude discrepancy with our value is difficult to explain. It is possible that our value could result from some sort of solution effect, but it seems more likely to us that the poor agreement may stem from the assumptions used by Schott and Davidson in correcting their coefficient down to room temperature or from pressure effects in their system.

4. A Mechanism to Explain the Material Balances and Detailed Decay Kinetics of NO_3 . To this point the kinetic data verify that process II provides the major pathway for the disappearance of NO_3 . However, values for k_{II} were determined using only the pseudo-first-order technique. If, indeed, process II alone accounted for all the second-order decay of NO_3 in those solutions, where no Ce^{III} is added prior to the flash, one should be able to use expression 10 and obtain values for $k_9 = k_{\text{II}}$ at each $[\text{HONO}_2]$. To test this

idea, the limiting slope absorbance data used for Table III were treated in terms of expression 10 by the method of least squares. Table IV summarizes the slopes, $(k_9/\epsilon_{\text{NO}_3}^{6350} l)$, obtained for each $[\text{HONO}_2]$ and the calculated values of k_9 which assume $\epsilon_{\text{NO}_3}^{6350} l = 1.87 \times 10^3 M^{-1}$. For comparison the k_{II} 's are also given. These were determined previously using the pseudo-first-order technique.^{2,10} Here one sees that in all four cases cited $k_9 \geq 1.3k_{\text{II}}$, which implies that some other process than (II) competes in the consumption of NO_3 in the absence of $[\text{Ce}^{\text{III}}]_{\text{A}}$. This result was anticipated earlier, when it was pointed out that the kinetic orders for the decay data from the same four cases were always slightly less than 2.0 (see Table III).

Partial evidence for a secondary reaction of NO_3 was presented earlier by Martin, *et al.*⁴ They found that the exposure of dilute Ce^{IV} solutions in 6.0 M HONO_2 to many successive flashes produced some permanent bleaching of the Ce^{IV} absorption. In explaining these results the following abstraction by "hot" NO_3 radicals excited by excess photon or reaction energy was proposed



from which it was postulated that perhaps secondary reaction by hydrogen peroxide formed by the dimerization of OH radicals could account for the observed bleaching. Since process 13 competed with process II, it was presumed that $k_{13}[\text{H}_2\text{O}] \ll k_{\text{II}}[\text{Ce}^{\text{III}}]_{\text{F}}$, because the secondary reaction of NO_3 did not interfere with the pseudo-first-order technique for the measurement of k_{II} . From thermochemical data they estimated the heat of reaction for process 13 to be <14 kcal/mol (25°).

This earlier interpretation is now known to be false as we shall show below. Consequently we set out to find a new secondary process which could compete with (II) in consuming NO_3 and which would also explain this important bleaching reaction. Several experiments were designed to obtain more quantitative information about the permanent bleaching process. We reasoned that a better understanding of those parameters influencing the bleaching reaction might shed light on the mechanism of the NO_3 decay kinetics. To this end, the effects of varying temperature, $[\text{Ce}^{\text{III}}]_{\text{A}}$, and $[\text{HONO}_2]$ on the efficiency of the bleaching reaction were studied. The results will now be presented, followed by the mechanistic implications which they produced.

The change in $[\text{Ce}^{\text{IV}}]$ per flash was determined at three temperatures: 0.5, 24, and 75° . Each run was conducted on a fresh sample of the same $1.99 \times 10^{-3} M$

(23) G. Schott and N. Davidson, *J. Amer. Chem. Soc.*, **80**, 1841 (1958).

Table V. Summary of Data from the Ce^{IV} Bleaching Study in Aqueous HONO₂ Solutions

Temp, °C	[HONO ₂] _A , M	[Ce ^{III}] _A × 10 ³ , M	[Ce ^{IV}] × 10 ³ , M	Δ log I ₀ /I ± σ ^a × 10 ²	Δ[Ce ^{IV}] ± σ ^b × 10 ⁵ , M
0.5	2.00	0.00	1.99	5.21 ± 0.25	10.3 ± 0.50
24	2.00	0.00	1.99	5.52 ± 0.10	10.9 ± 0.20
75	2.00	0.00	1.99	5.09 ± 0.48	10.1 ± 0.90
25	2.00	3.95	1.11	3.86 ± 0.20	4.29 ± 0.22
25	2.00	4.88	1.12	3.54 ± 0.10	3.97 ± 0.11
25	2.00	7.27	1.13	3.37 ± 0.06	3.81 ± 0.07
25	2.00	8.02	1.10	3.25 ± 0.09	3.58 ± 0.10
25	2.00	10.35	1.13	3.11 ± 0.08	3.51 ± 0.09
25	2.00	0.00	2.17	4.92 ± 0.19	10.7 ± 0.40
25	7.98	0.00	0.525	17.2 ± 0.60	9.02 ± 0.30
25	14.00	0.00	0.505	16.5 ± 0.40	8.34 ± 0.21

^a Change in Ce^{IV} absorbance per flash. ^b Change in [Ce^{IV}] per flash.

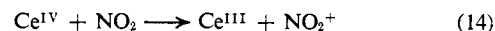
Ce^{IV} solution in 2.00 M HONO₂. The results of this study are shown in the first section of Table V. Here it is seen that a change in temperature from 0.5 to 75° produces essentially no change in the amount of Ce^{IV} bleached within the limits of experimental error. Using the estimated value of Δ*H*₂₉₈ < 14 kcal/mol for process 13, one might calculate that in going from 0.5 to 75° the ratio, *k*₁₃(75°)/*k*₁₃(0.5°), should be <250. With such a change in the rate of reaction 13, one would expect to see some temperature effect; however, the change in [Ce^{IV}] was clearly temperature independent.

The change in [Ce^{IV}] per flash was determined as a function of [Ce^{III}]_A. Each run was conducted on a fresh sample of 1.0 × 10⁻³ M Ce^{IV} and an appropriate concentration for [Ce^{III}]_A in 2.00 M HONO₂ solutions at 25 ± 1°. The results of this study are shown in the second section of Table V. It is seen that the increase in [Ce^{III}]_A leads to a net decrease in the quantity of Ce^{IV} bleached. This supports the contention that the mechanism by which Ce^{IV} becomes permanently reduced is one which competes with process (II) in the consumption of NO₃. In view of this fact, one would think that the competing reaction must be a secondary process following the generation of NO₃ and, hence, is not the result of a parallel primary photochemical step, such as (3).

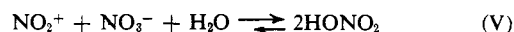
The change in [Ce^{IV}] per flash was determined at 2.00, 7.98, and 14.0 M HONO₂. Each run was conducted on a fresh sample, the [Ce^{IV}] of which was adjusted so that the absorbance curves at each concentration were essentially identical. The results of this study are shown in the third section of Table V, where it is seen that the quantity of Ce^{IV} permanently bleached decreases with increasing [HONO₂]. Since *k*₁₁ was shown previously¹⁰ to increase over this range of increasing [HONO₂], further support is given to the possibility that the bleaching reaction is a secondary reaction competing with (II).

To elucidate the exact stoichiometry and material balances involved in the bleaching reaction, several micromolar gas analyses (see Experimental Section) were conducted to determine if any gaseous products were formed. A measured quantity of 1.5 μmol of O₂ was produced with 38.5% bleaching of the original Ce^{IV} solution. Comparing the quantity of Ce^{IV} bleached to O₂ produced in μmoles gave the following ratio: Δ[Ce^{IV}]/O₂ = 6.14/1.50 = 4.08. A similar experiment using thoroughly degassed 2.00 M HONO₂ solution without any Ce^{IV} added was found to produce no O₂; hence, O₂ does not arise from the direct pho-

tolysis of the background solvent. Upon guessing various bleaching mechanisms the possible involvement of intermediate NO₂ was considered. Qualitative tests in which NO₂ was bubbled through Ce^{IV}-HONO₂ solutions showed an instantaneous bleaching of the ceric yellow color. To better gauge the stoichiometry of this reaction, exactly 4.00 ml of 5.05 × 10⁻³ M Ce^{IV} in 2.00 M HONO₂ solution was treated with 8.14 μmol of NO₂ using standard vacuum transfer techniques. The change in Ce^{IV} was 40.8%. This was equivalent to 8.24 μmol of Ce^{IV} reduced. Comparing this value with the NO₂ added, one obtains the ratio Δ[Ce^{IV}]/NO₂ = 8.24/8.14 = 1.01. The reaction of NO₂ with Ce^{IV} in the aqueous HONO₂ solution has been interpreted by Johnson and Martin²⁴ in terms of the electron transfer process



producing the nitronium ion. At the higher [HONO₂] used in this study, NO₂⁺ is rapidly consumed by excess nitrate ions and water by the process



It is of interest that (V) becomes reversible in solutions where [HONO₂] > 11.0 M and the reverse reaction displays an apparent activation energy of 8 kcal/mol.²⁴ At these concentrations small quantities of NO₂⁺ exist through "self-ionization"¹⁸ of HONO₂.

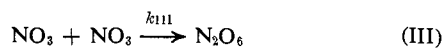
To summarize the above results, any mechanistic scheme which explains both the spontaneous electron transfer process (II) and a process by which Ce^{IV} becomes permanently bleached to Ce^{III} must fit the following experimental constraints. (a) The overall mechanism must explain the essentially bimolecular decay of NO₃ in the absence of [Ce^{III}]_A with a rate constant *k*₉ ≥ 1.3*k*₁₁ at a given value for HONO₂. (b) The process by which Ce^{IV} is bleached must be temperature independent. (c) The bleaching reaction must explain the decrease in the quantity of Ce^{IV} bleached with increasing [Ce^{III}]_A. (d) The bleaching reaction must explain the decrease in the quantity of Ce^{IV} bleached with increasing [HONO₂]. (e) The products of the bleaching reaction must contain Ce^{III} and oxygen in a stoichiometric ratio of 4:1, respectively. (f) If NO₂ is formed in the mechanism, it must reduce Ce^{IV} to Ce^{III} with a stoichiometric ratio of 1:1, respectively.

With these constraints in mind a number of possible mechanisms were considered,² e.g., the competitive

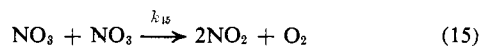
(24) R. W. Johnson and D. S. Martin, Jr., *J. Inorg. Nucl. Chem.*, **10**, 94 (1959).

formation of NO_3 and OH radicals in two parallel primary processes, the fractional dissociation of NO_3 in the primary process, and the thermal and photodissociation of NO_3 subsequent to the primary process. While such mechanisms qualitatively provide plausible explanations for the Ce^{IV} bleaching, none could be blended to give satisfactory agreement with the known chemical facts and the overall NO_3 decay data. Furthermore, the value of $[\text{NO}_3]_{t=0} = 0.86 \times 10^{-3} M$ determined from the pseudo-first-order runs in 2.00 M HONO_2 , when compared to the total amount of Ce^{IV} reduced in similar solutions (see Table V), showed that the competitive bleaching process accounted for only a small fraction of the overall NO_3 decay, a fact which is consistent with the observed lack of interference of the bleaching process in the pseudo-first-order measurements.^{4,10} From the same data we also inferred that the bleaching reaction must slowly introduce excess Ce^{III} into the reaction system as the NO_3 decay proceeds. For in this way we could explain the increasing deviations from the second-order kinetics as the imbalance of $[\text{Ce}^{\text{III}}]$ and $[\text{NO}_3]$ increased. Noting that the second-order constant $k_9 \geq 1.3k_{\text{II}}$, but that the decay still obeys fairly good second-order kinetics in terms of expression 9, suggested that the bleaching process was also second order with respect to NO_3 , such that k_9 represents a compounded rate constant for both processes.

With these ideas in mind, we reported¹ that the most suitable rate-limiting step to explain the concurrent bleaching reaction was the radical dimerization process



There is certainly precedent^{23,25} for this reaction in the gas phase. Schott and Davidson²³ studied NO_3 arising from the shock pyrolysis of N_2O_5 and were able to derive a rate constant and activation energy at 300°K for the process

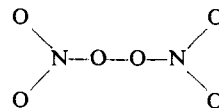


where $k_{15} = 1.3 \times 10^5 M^{-1} \text{sec}^{-1}$ and $E_a = 6.0 \pm 2.5$ kcal/mol. Also, Daniels⁸ has recently used our suggestion of this reaction in explaining his results on the second-order decay of NO_3 in HONO_2 solutions following pulse electron radiolysis. Process 15 can be used to explain the bleaching effect in the present solution study, because NO_2 would reduce $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$ by process 14 and the net $\text{Ce}^{\text{III}}/\text{O}_2$ ratio would be 4/1 as found. However, our bleaching process was shown to be temperature independent, while process 15 involves a necessary activation energy. Since most free-radical combination reactions display activation energies near zero, it would be justifiable to assume that the NO_3 dimerization process (III) itself would be essentially unimpeded by an energy barrier. Hence, it must be the N-O bond breaking and O-O bond formation in the transition state of process 15 for which energy is needed. Since the unpaired electron in NO_3 completely resides on an oxygen atom,²⁶ the

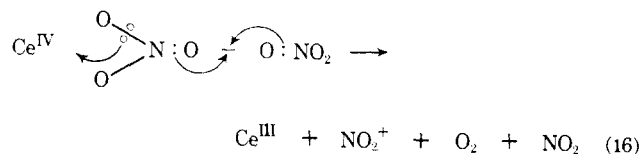
(25) H. S. Johnston, *J. Amer. Chem. Soc.*, **73**, 4542 (1951).

(26) G. W. Chantry, A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **5**, 589 (1962); R. M. Golding and M. Henchman, *J. Chem. Phys.*, **40**, 1554 (1964); R. Livingston and H. Zeldes, *ibid.*, **41**, 4011 (1964).

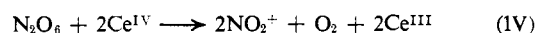
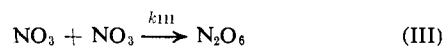
probable configuration for the bonding in the intermediate dimer would be



Then to explain the apparent lack of an activation energy in the process which leads to the permanent bleaching of Ce^{IV} , we must postulate that the decomposition of the $\text{O}_2\text{N-O-O-NO}_2$ dimer occurs at the expense of the ≈ 1.6 eV of energy latent in the $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$ couple in HONO_2 solutions.²⁷ The overall process might be represented as follows

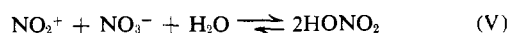
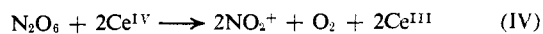
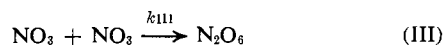
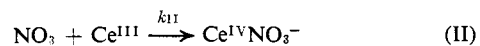
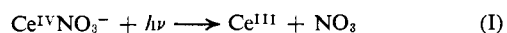


It is worth noting that the overall reduction of Ce^{IV} by the proposed dimer is formally analogous to the reduction of Ce^{IV} by hydrogen peroxide in acid solutions. Using labeled hydrogen peroxide, it has been shown²⁸ that the oxygen produced upon reduction of Ce^{IV} in aqueous acid solutions is derived entirely from the peroxide, showing that the O-O bond remains unbroken. Similarly, we would predict that the O_2 produced in process 16 arises from the peroxide linkage in the dimer. The NO_2 resulting from (16) is rapidly reduced by a second Ce^{IV} species, such that the entire sequence might be written as



wherein the rate-limiting step for steric reasons is the dimerization process III.

Guided by these arguments and in accord with all of our data, we believe the overall NO_3 decay mechanism in 1-15 M aqueous HONO_2 solution at room temperature should be reported as



This mechanism explains the generation of NO_3 and provides concurrent processes II and III which compete in consuming NO_3 over the entire decay period. The observed Ce^{IV} bleaching results from the temperature-independent sequence III-IV. It also satisfies all of the experimental constraints which were listed above.

On the basis of this mechanism, a rate expression for the disappearance of NO_3 can be written with the assumption that $k_{\text{II}} \gg k_{\text{III}}$ such that the quantity $[\text{N}_2\text{O}_6]$ is always very small. The desired rate expression becomes

$$-d[\text{NO}_3]/dt = k_{\text{II}}[\text{Ce}^{\text{III}}][\text{NO}_3] + 2k_{\text{III}}[\text{NO}_3]^2 \quad (17)$$

(27) G. F. Smith and C. A. Getz, *Anal. Chem.*, **10**, 191 (1938).

(28) W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide," American Chemical Society Monograph No. 128, Reinhold, New York, N. Y., 1955, pp 376, 386.

With excess Ce^{III} in the solution prior to the flash, the second term becomes negligible and expression 17 reduces to (6) used in the pseudo-first-order kinetic study. Unfortunately, expression 17 does not yield a simple integrated solution. The first term leads to a disappearance of Ce^{III} from the system, while the second term leads to an increase in Ce^{III} due to the bleaching sequence III-IV. Because of these complications, plus the fact that only the change in $[\text{NO}_3]$ can be precisely monitored during the course of the reaction, it becomes obvious that some simplification of eq 17 is necessary in order to estimate k_{III} . Looking again at the flash kinetic runs in which there is no $[\text{Ce}^{\text{III}}]_{\text{A}}$, one recalls that the decay data were treated with some success in terms of expression 9 where it was assumed that $[\text{Ce}^{\text{III}}]_t = [\text{NO}_3]_t$. Plots of the data from runs in 3.5, 8.00, 13.0, and 15.0 M HONO_2 solutions were linear for the initial portion of the decay curves and began to show increasing deviations from linearity at longer times. In view of the proposed mechanism, it is obvious that $[\text{Ce}^{\text{III}}]_t \neq [\text{NO}_3]_t$ at longer times, and as the reaction proceeds $[\text{Ce}^{\text{III}}]$ becomes increasingly greater than $[\text{NO}_3]$. However in the limit where $[\text{Ce}^{\text{III}}]_t \simeq [\text{NO}_3]_t$ in the initial portion of the curves, an estimate for the value of k_{III} might be obtained by reducing (17) to the form

$$-d[\text{NO}_3]/dt = (k_{\text{II}} + 2k_{\text{III}})[\text{NO}_3]^2 = k_9[\text{NO}_3]^2 \quad (18)$$

i.e., the same form as eq 9. To test the idea expressed by this relationship, the values of k_9 and k_{II} given in Table IV were used. At each $[\text{HONO}_2]$ the values of k_{III} given in the last column of Table IV were obtained from the relationship $k_{\text{III}} = (k_9 - k_{\text{II}})/2$.

The estimated k_{III} 's are seen to remain essentially constant while k_{II} varies upon changing $[\text{HONO}_2]$. That the rate of NO_3 dimerization should be inde-

pendent of $[\text{HONO}_2]$ is not too surprising. NO_3 is symmetric and uncharged and its absorption spectrum remains essentially unchanged in going from 1.00 to 15.0 M HONO_2 , so there is little reason to expect a solvent interaction with this radical. Assuming that the dimerization rate constant is independent of $[\text{HONO}_2]$, the average value of k_{III} from Table IV is $(0.79 \pm 0.04) \times 10^8 M^{-1} \text{sec}^{-1}$ at $25 \pm 1^\circ$. It is recalled that Schott and Davidson²³ gave an estimated value for the dimerization rate constant as $k_{15} = 0.13 \times 10^6 M^{-1} \text{sec}^{-1}$ at 300°K in the gas phase. The fact that $k_{\text{III}} \simeq 6k_{15}$ is not too surprising. In the gas phase the rate of dimerization of NO_3 radicals involves not only steric factors in the formation of the transition state dimer, but also an activation energy for the bond-breaking and -making processes which must occur before product formation. In this study, the rate of dimerization involves primarily steric considerations, with the energy necessary for the dimer decomposition being contained in the potential energy of the $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$ transition. With these factors in mind, the agreement between k_{III} and k_{15} seems quite acceptable. However, Daniels's⁸ estimate of $4.2 \times 10^8 M^{-1} \text{sec}^{-1}$ for k_{III} from pulsed radiolysis results is puzzling. This value is much higher than ours and cannot be justified in this system with the magnitude of k_{II} .

In conclusion, the only weakness we know of in the proposed mechanism is the fact that the presence of N_2O_6 has not been proven on the basis of direct spectroscopic evidence. We rely on the total consistency of all kinetic and material balance data to postulate its key involvement in the bleaching process. Finally, we are now content that much of the earlier confusion over the behavior of the NO_3 radical in this solvent system is well enough resolved from this work to move on to other problems.

Crystal Structure and Properties of Barium Nickel Sulfide, a Square-Pyramidal Nickel(II) Compound¹

I. E. Grey and H. Steinfink

Contribution from the Materials Science Laboratory, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712. Received February 27, 1970

Abstract: The compound BaNiS_2 crystallizes in the tetragonal system, space group $P4/nmm$, with lattice constants $a = 4.430$ (1), $c = 8.893$ (2) Å. Its structure consists of puckered two-dimensional layers of edge-sharing square-pyramidal $[\text{NiS}_4]^{2-}$ polyhedra parallel to (001), with barium atoms packing between the layers. Within a square-pyramidal unit, the Ni-S (axial) bonds of length 2.316 (5) Å are slightly shorter than the Ni-S (equatorial) bonds, of length 2.345 (2) Å. Electrical resistivities and magnetic susceptibilities were measured as a function of temperature and the results indicate that the compound is metallic. The nearly temperature-independent susceptibility is due to Pauli paramagnetism.

A large number of five-coordinated nickel(II) compounds have now been characterized by detailed X-ray structural analyses.²⁻⁶ In these compounds, the

five-coordination is generally achieved by using bulky, multidentate organic ligands. Very recently a nickel(II)

(1) Research sponsored by the Robert A. Welch Foundation, Houston, Texas.

(2) (a) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **8**, 1915 (1969).

(b) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 206, (1970).

(3) P. L. Orioli and M. Di Vaira, *ibid.*, **A**, 2078 (1968).

(4) M. Di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B*, **24**, 595 (1968).

(5) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).

(6) F. K. Ross and G. B. Stucky, *Inorg. Chem.*, **8**, 2734 (1969).