added. Separation of the volatile products by glpc gave 0.03 mmol of 2-$BrC_2B_5H_6$ and 0.17 mmol of $C_2B_5H_7$. The mass spectrum of the 2-bromo derivative contains an intense parent grouping, with a sharp cutoff at *m/e* 166 corresponding to the $^{81}Br^{12}C_2{}^{11}B_5{}^1H_6^+$ ion. An almost equally intense grouping with a cutoff at *m/e* 85 indicates substantial cleavage of the C–Br bond in the spectrometer (in contrast, the mass spectrum of 5-$BrC_2B_5H_6$ shows very little evidence of fragmentation other than hydrogen abstraction). The ir spectrum has absorptions at 2620 (vs), 1195 (s), 1080 (s), 1030 (s), 890 (m), 835 (m), 810 (s), 780 (sh), and 710 (s) cm^{-1}.

The ^{11}B nmr spectrum (CS_2 solution) confirms the bromine substitution at C(2), since none of the doublets arising from B–H coupling in the spectrum[17,18] of 2,4-$C_2B_5H_7$ is collapsed, and B(5)–H and B(6)–H are rendered nonequivalent. Partially overlapped doublets, each of area 1, are centered at δ −9.0 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (J = 186 Hz), δ −8.0 ($J \sim$ 160 Hz), and δ −3.2 ($J \sim$ 160 Hz). Comparison with the spectrum[17,18] of unsubstituted 2,4-$C_2B_5H_7$ suggests that these resonances arise from B(3)–H, B(5)–H, and B(6)–H, respectively, although these assignments are equivocal at present. A doublet of area 2, centered at δ +17.5 (J = 186 Hz), is uniquely assigned to the equivalent B(1)–H and B(7)–H bonds.

Degradation of 2,4-Dicarba-*closo*-heptaborane(7) by Alcoholic Base. A mixture of 1.0 mmol of $C_2B_5H_7$ and 3.0 mmol of potassium hydroxide in absolute ethanol was stirred at −31° for 6 hr, during which 0.1 mmol of H_2 was evolved. The temperature was raised to −23° and then to −16°, at which the rate of H_2 evolution was appreciable. The mixture was stirred at −16° for 75 hr, which gave an additional 1.26 mmol of H_2. Subsequent reaction periods of 70 hr at 0°, 60 hr at 25°, and 20 hr at 50° liberated 3.71, 0.72, and 0.16 mmol of H_2, respectively. After removal of all solvent, which contained no detectable volatile products as shown by glpc analysis, the remaining solid material was suspended in pentane and treated with 6.8 mmol of anhydrous HCl. Glpc analysis of all volatile materials gave 2.9 mmol of HCl, 2.0 mmol of H_2O, and 0.78 mmol of triethoxyborane, which was identified from its ir, proton nmr, and mass spectra. Ir analysis of the remaining solid indicated only boric acid.

Acknowledgments. We thank Dr. R. E. Williams of the Aerojet-General Corporation for a generous gift of a mixture of the lower caboranes. This work was supported by the Office of Naval Research.

---

[17] T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Amer. Chem. Soc.*, **88**, 4622 (1966).

[18] R. N. Grimes, *ibid.*, **88**, 1895 (1966).

Competitive Electron Transfer. Activity-Defined Formation Constants of Cerium(III) Nitrate Complexes Based on Reaction with the Nitrate Free Radical[1]

T. W. Martin[2] and R. W. Glass

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

Abstract: The rate constant (k_{11}) for the bimolecular electron-transfer process, $Ce^{III} + NO_3 \rightarrow Ce^{IV}NO_3^-$, was measured by a kinetic flash photolysis method at 25 ± 1° in aqueous solutions with stoichiometric concentrations of nitric acid ([$HONO_2$]) ranging from about 10^{-3} to 15 *M*. The observed k_{11}'s were correlated against the activity of undissociated $HONO_2$ (a_u) to keep all changes in solvent composition on the same definable basis. The functional behavior suggested by this correlation was interpreted by a theoretical–chemical model which presumes the participation of different Ce^{III} complexes, each of which competes in consuming NO_3 at a fixed specific rate (k_i) and whose relative concentrations are controlled by the $HONO_2$ environment. It is shown that no fewer than four formation constants (K_0, K_1, K_2, and K_3) interrelating five different Ce^{III} species (C_0, C_1, C_2, C_3, and C_4) are required to fit the data for nitrate solutions where $[H^+] \geq 1.0$ *M*, and that each formation constant (K_i) is described by an equilibrium of the simple stoichiometric form $C_i + a_u = C_{i+1}$. It is significant that this experimental approach defines a set of thermodynamic K_i's which are constant over the entire a_u range, eliminating their usual dependence upon ionic strength and making it possible to evaluate formation constants in concentration ranges hitherto inaccessible by other methods. Evidence is given to show that the "bare" hydrated Ce^{III} species is not possible in this solvent system and that C_0 possesses at least one nitrate ligand. Arguments are given to explain the trends and relative sizes of the k_i's and to explain why they are so far from the diffusion-controlled limit. It remains to be shown whether this new method of estimating formation constants based upon a spontaneous *competitive electron transfer* among structurally different metal complexes and a free radical can be extended to other systems.

In an earlier communication[3] we proved that the NO_3 free radical can be generated efficiently at room temperature by the photolysis of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, dissolved in aqueous $HONO_2$ solution. Without information about the exact structures of the Ce^{IV} and Ce^{III} complexes involved, the primary photochemical process was represented by a generalized notation as

$$Ce^{IV}NO_3^- + h\nu \longrightarrow Ce^{III} + NO_3 \qquad (I)$$

to suggest that the radical is released to the solution following an intramolecular electron transfer in the excited Ce^{IV} complex. Contrary to opinion expressed elsewhere[4] that the NO_3 in this system arises from the

---

[1] This work was made possible by the U. S. Atomic Energy Commission (Contract No. AT-(40-1)-2825) and the National Science Foundation (Grant No. GP-2671). R. W. G. is indebted for personal support to the U. S. Steel Foundation and for a Public Health Service Fellowship (No. F1-GM-28, 402) from the National Institute of General Medical Sciences. We are grateful to R. C. Gross for conducting some preliminary experiments, to Dr. R. E. Rummel for drawing Figure 1, and to Dr. L. J. Schaad for assistance in computer programming. T. W. M. also wishes to thank Drs. G. R. Choppin, H. M. Neumann, and B. A. Soldano for their contributions to the success of this research.

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

direct photolysis of the $HONO_2$ solvent, we are convinced that the Ce^{IV} complex is directly involved in producing this radical. Furthermore, we believe that only process I is necessary to explain the generation of NO_3 in our experiments because there is no physical evidence for another radical precursor to NO_3, such as the OH radical postulated by other workers.[5] A review of the data in support of these conclusions and a detailed discussion of possible mechanistic interpretations for process I are given in a separate paper.[6]

Using a kinetic flash photolysis method,[7] we further showed that all possible secondary reactions of NO_3 are in competition with the fast spontaneous bimolecular electron-transfer process

$$Ce^{III} + NO_3 \xrightarrow{k_{II}} Ce^{IV}NO_3^- \qquad (II)$$

which in the absence of added competitive reactants is the major pathway for the disappearance of NO_3 in this system. In 6.0 *M* aqueous $HONO_2$ we reported $k_{II} = (1.70 \pm 0.04) \times 10^6\ M^{-1}\ sec^{-1}$ at 23° and estimated the apparent activation energy (E_a) to be only 1.0 ± 0.2 kcal/mol. Interpreting these results by means of the simple collision theory expression, $k_{II} = pZe^{-E_a/RT}$, where p is the empirical steric factor and Z the bimolecular collision number, it is obvious from the size of E_a that a significant steric factor ($p \simeq 10^{-4}$–10^{-5}) must be assigned because k_{II} is four to five orders of magnitude smaller than would be expected for a diffusion-controlled reaction (*i.e.*, $k_{II} \simeq Z$).

When it was discovered that k_{II} quantitatively increased about an order of magnitude with increasing $[HONO_2]$, it became convenient to consider p as some function of two probability terms: a very large primary steric factor (p_1), which accounts for the major structural problem preventing k_{II} from reaching a diffusion-controlled upper limit, and a small secondary steric factor (p_2), which covers the specific structural influences of the $[HONO_2]$ on k_{II}.

Following this rather arbitrary but experimentally defined separation into two kinds of steric factors, we undertook to measure k_{II} precisely in a series of aqueous solutions having progressively increasing $[HONO_2]$ ranging from about 10^{-3} to 15 *M*. We hoped from these data, first of all, to deduce the correct structural origin for p_2. Secondly, we hoped that once this p_2 effect was understood it might provide sufficient insight to guess the nature of the special stereochemical problem contained in the p_1 term. The general purpose of this paper is to show to what extent these hopes have materialized and, in particular, to explain why we believe from our interpretation of the p_2 effect that the very symmetric and electrically neutral NO_3 radical must act as an effective "kinetic microprobe" of structurally different Ce^{III} species in solution—a phenomenon we have labeled *competitive electron transfer.*

Experimental Section

1. **Chemicals and Sample Solutions.** The "primary standard grade" ceric ammonium nitrate (G. F. Smith Chemical Co.) was used directly after drying for 2 hr at 85° and stored in a desiccator over silica gel prior to weighing for sample preparation. Hydrated cerous ammonium nitrate (G. F. Smith Chemical Co.) was used directly from the reagent bottle. The concentrations of $HONO_2$ and $HOClO_3$ stock solutions were adjusted and standardized against carbonate-free sodium hydroxide of known strength.

The preparation of the Ce^{IV} and Ce^{III} stock solutions in $HONO_2$ essentially followed the techniques used in previous work.[7] Each Ce^{IV} or Ce^{III} salt sample was weighed and separately dissolved in stock $HONO_2$ solvent of the desired concentration. Since the Ce^{III} salt is not a primary standard, the exact $[Ce^{III}]$ of each stock solution was determined gravimetrically by firing an aliquot and weighing the CeO_2. Aliquots of these two stock salt solutions were then combined to give the final sample solution. The slow oxidation of Ce^{III} to Ce^{IV} in $[HONO_2] > 10\ M$ (studied elsewhere[8]) placed stringent requirements on the use of fresh stock solutions. Hence, the flash runs were made as soon as possible after dissolving and diluting the salt samples. A careful check showed that within the usual time of about 40 min to perform a set of six kinetic runs the decrease in $[Ce^{III}]$ and corresponding increase in $[Ce^{IV}]$ (at 25 ± 1°) was negligible for our purposes.

The $HOClO_3$ solutions were prepared by diluting weighed salt samples to approximately $1 \times 10^{-3}\ M$ in Ce^{IV} and $4 \times 10^{-3}\ M$ in Ce^{III} to be consistent with the $HONO_2$ work. However, it was found at these salt concentrations when $[HOClO_3] < 3\ M$ that the efficiency of NO_3 generation was too low for good kinetic measurements. This problem was overcome for the experiments in 1.52, 2.03, and 2.50 *M* $HOClO_3$ (see Table II) by increasing the concentrations of both salts by about a factor of 2. The exact $[Ce^{III}]$ for the $HOClO_3$ stock solutions was determined gravimetrically.

2. **Optical System and Electronic Apparatus.** The same optical and electronic techniques were used as described in previous work.[7] The entrance and exit slit widths of the monochromator were set at 2.6 mm to monitor the most sensitive NO_3 absorption band at 635 ± 8 nm.

3. **Data Processing.** Evaluation of the kinetic data in this paper differed from previous work[7] primarily in the application of computer techniques for making least-squares analyses of the many NO_3 decay curves and in solving related statistical problems. Experimental conditions were arranged so that each decay curve obeyed the simple rate expression $-d[NO_3]/dt = k'[NO_3]$, by means of which the pseudo-first-order rate constant k' was evaluated directly from the kinetic data. The experimental bimolecular rate constant k_{II} corresponding to each k' was calculated using the relationships $[Ce^{III}]_E = [Ce^{III}]_A + [Ce^{III}]_G$ and $k' = k_{II}[Ce^{III}]_E$, where $[Ce^{III}]_E$ represents the average *effective* concentration over the measured decay time, $[Ce^{III}]_A$ is the initial concentration *added* before the flash, and $[Ce^{III}]_G$ is an empirical correction factor (defined below) which accounts for the Ce^{III} *generated* by the flash and averaged over the measured time interval.

Every experimental rate constant reported here is the computed average for a set of six individual flash runs, each made under identical conditions on a fresh portion of the same sample solution. A run in this work consisted of making two oscillograms. The first, taken prior to the photolysis flash, was a trace of the full-light intensity (I_0) transmitted by the sample over a preselected interval on the oscilloscope time scale (D). The second, begun at 50 μsec after triggering the flash lamp discharge, was a trace of the attenuated intensity (I) over the same time interval and constituted the true NO_3 decay curve. As in previous work, each oscillogram was recorded on 35-mm film from which an enlarged print superimposed by a millimeter grid system was obtained for making more precise measurements of the data point arrays (D, I) in time–intensity coordinates. In order to compensate for random noise in the trace, the array (D, I_0) measured from the first oscillogram consisted routinely of ten points uniformly spaced across the D axis; the average intensity ($\bar{I}_0$) for these points was taken as the true value for the run. The array (D, I) measured from each decay oscillogram consisted of 15–25 points all carefully duplicated at the same preselected D values for a period of two half-lives for each run.

In order to establish a consistent procedure for comparing the rate constants derived from different data sets, the following operational criteria were maintained in analyzing the decay curves from set to set: (a) no value of I was recorded at a time less than 15 μsec after triggering the oscilloscope sweep so as to allow time for electronic stabilization and to eliminate the effects of scattered light from the

---

[5] R. K. Broszkiewicz, *Int. J. Appl. Radiat. Isotop.*, **18**, 25 (1967); L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 71, 3802 (1967).

[6] R. W. Glass and T. W. Martin, *J. Amer. Chem. Soc.*, **92**, 5084 (1970).

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

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

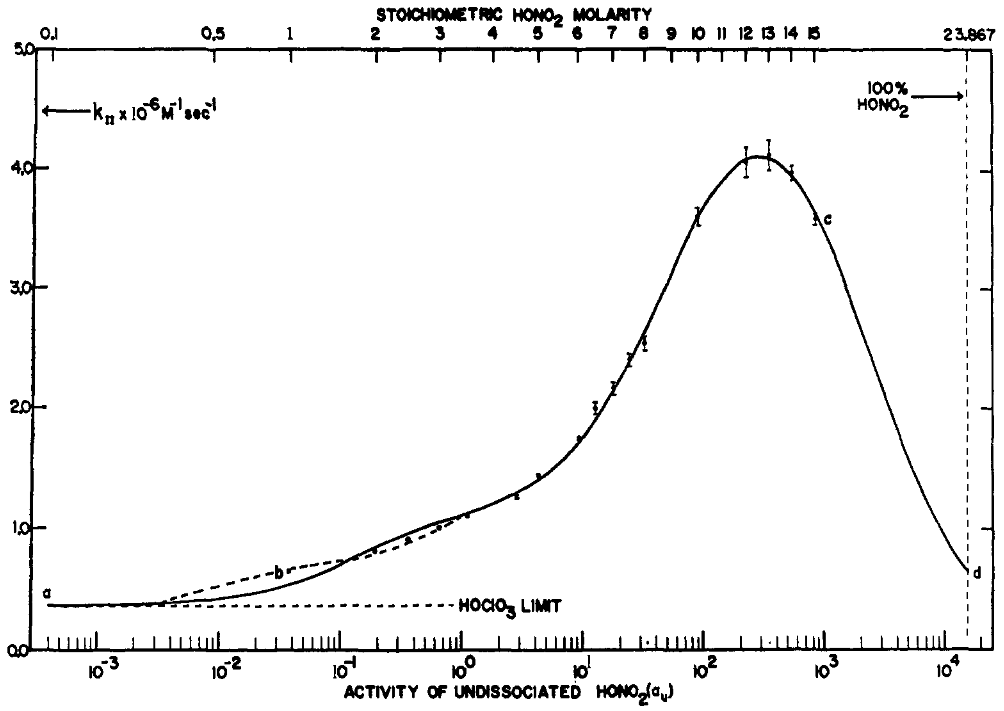

Figure 1. Plot of k_{II} data *vs.* activity of undissociated $HONO_2$ (a_u). Solid curve represents fit of the "four complex" model. Dashed curve shows variation introduced by the "five complex" model.

photolysis flash, (b) only those values of transmittance ($I/\bar{I}_0$) in the range of $0.1 < (I/\bar{I}_0) < 0.9$ were measured so as to minimize the effect of reading errors at both ends of the data range, and (c) within the preceding limits, the proper oscilloscope sweep speed and vertical deflection were selected for each set so as to provide the optimum display of the decay curve for the recording of at least two half-lives beginning at $I/\bar{I}_0 > 0.1$.

In analyzing the decay data, it was necessary to convert from the oscilloscope time scale (D) to the NO_3 reaction time scale (t). In previous work we found that zero time ($t = 0$) for this apparatus occurs approximately 10 μsec after triggering the flash discharge and corresponds to the maximum in the photolysis flash intensity. Hence, the required time conversion relation was $t = FD + T$; t is the elapsed reaction time in μsec, F is the number of microseconds per unit oscillogram time scale division, D is the number of oscillogram time scale divisions to be converted, and T is the time interval between $t = 0$ and the start of the oscilloscope sweep (40 μsec in this work). It was also known from previous work that an effective 40% flash conversion of a 1.01×10^{-3} M Ce^{IV} solution produced an absorbance of 0.77 at $t = 0$. This information provided an empirical way within experimental error to correct each run for the Ce^{III} generated in the flash by the equation $[Ce^{III}]_G = (\log \bar{I}_0/I)_{t=0}(0.40 \times 10^{-3}/0.77)$, where the absorbance at $t = 0$ was obtained by extrapolation of the NO_3 pseudo-first-order decay curves.

4. Computer Programs. Three programs written in Fortran for the IBM 7072 computer were used to accomplish the kinetic results cited in this paper. Program I was given the specific parameters $[Ce^{III}]_A$, $\bar{I}_0$, T, and F plus the raw kinetic data array (D, I) for each run in a set. It then accomplished the necessary averaging and least-squares analyses to obtain $(\log \bar{I}_0/I)_{t=0}$, $[Ce^{III}]_G$, k', and k_{II} with standard deviations. Program II was used to obtain the best curve fit of the theoretical rate constant k_{II}^* defined by eq 5 from the experimental k_{II}'s as displayed in Figure 1. This program employed the method of "pattern search"[9] which by successive iterations minimizes the function of the residuals

$$R = \sum_{j=1}^{n}[(k_{II})_j - (k_{II}^*)_j]^2$$

where n is the total number of independent observations. In eq 5 both a_u and k_I were taken as known. The value of k_I was fixed at 0.355×10^6 M^{-1} sec^{-1} (see Table II), while the values of the six adjustable parameters k_2, k_3, k_4, K_1, K_2, and K_3 were subjected to the pattern search procedure in order to find their best values as reported in Table III. Substituting the derived constants listed in Table III into eq 5, the standard deviation of the set of n "observational equations" with regard to all observations becomes

$$\sigma_{k_{II}^*} = [R/(n - m)]^{1/2} = 5.90 \times 10^4\ M^{-1}\ \text{sec}^{-1}$$

where R is the sum of the square deviations given above and m is the number of adjustable parameters. The difference ($n - m$) represents the number of degrees of freedom for the system; in this work $(n - m) = (17 - 6) = 11$. Program III was necessary to determine the standard deviations (±σ's) reported in Table III for the constants derived by program II. Using a standard least-squares method,[10] a set of normal equations was constructed from eq 5 in terms of the variables k_2, k_3, k_4, K_1, K_2, and K_3. By computing the inverse of the coefficient matrix of this set of equations, the standard deviation σ_i of the ith variable was found by means of "external consistency,"[11] that is

$$\sigma_i^2 = (M)_{ii}^{-1}(\sigma_{k_{II}^*})^2$$

where $(M)_{ii}^{-1}$ represents the diagonal elements of the inverse of the coefficient matrix and $(\sigma_{k_{II}^*})^2$ is the square of the standard deviation of the observational equations defined above.

Results

1. Variation of k_{II} with $[HONO_2]$. The results of the pseudo-first-order kinetic study are summarized in Table I with the standard deviations reflecting uncertainties caused primarily by noise in the oscilloscope decay curves. Upon proceeding from 1.0 to 15.0 M $HONO_2$ solutions, the value of k_{II} is seen to vary almost an order of magnitude, with a maximum at about 13 M $HONO_2$.

Intuitively, the easiest way to rationalize the influence of $[HONO_2]$ in these systems was to presume that $HONO_2$ acts through a series of formation equilibria to

---

[9] D. J. Wilde, "Optimum Seeking Methods," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 145; subroutine by M. E. Schwartz, Ph.D. Thesis, Vanderbilt University, 1966, Appendix II.

[10] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, Van Nostrand, New York, N. Y., 1964, p 517.

[11] J. W. M. DuMond and E. R. Cohen, *Rev. Mod. Phys.*, **25**, 691 (1953).

Table I. Summary of Pseudo-First-Order Study in Aqueous $HONO_2$ Solutions at 25 ± 1°

$[HONO_2]$, M	$[Ce^{IV}] \times 10^3$ M	$[Ce^{III}]_A \times 10^3$ M	Half-life, μsec	$k' \times 10^{-3}$ sec^{-1}	$k_{II} \pm \sigma^a \times 10^{-6}$ M^{-1} sec^{-1}	$\pm\sigma$, %
1.00	1.00	4.00	250	2.77	0.641 ± 0.011	1.7
2.00	1.00	3.95	195	3.53	0.744 ± 0.015	2.0
2.50	0.99	4.00	164	4.23	0.917 ± 0.009	1.0
3.00	0.99	4.00	142	4.87	1.010 ± 0.010	1.0
3.50	1.01	3.90	129	5.38	1.110 ± 0.015	1.4
4.50	1.00	4.05	114	6.10	1.270 ± 0.022	1.7
5.00	1.00	4.00	99	7.04	1.440 ± 0.013	0.9
6.00	0.99	4.00	79	8.83	1.750 ± 0.012	0.7
6.50	1.00	3.93	75	9.27	1.980 ± 0.046	2.3
7.00	1.00	3.87	68	10.20	2.170 ± 0.051	2.4
7.50	1.00	3.91	61	11.40	2.410 ± 0.048	2.0
8.00	1.00	4.00	56	12.50	2.550 ± 0.066	2.6
10.00	1.00	4.00	39	17.70	3.610 ± 0.071	2.0
12.00	0.99	4.00	35	19.90	4.070 ± 0.120	3.0
13.00	1.00	4.01	34	19.60	4.130 ± 0.130	3.2
14.00	0.99	4.00	36	19.40	3.980 ± 0.062	1.6
15.00	1.00	3.91	42	16.70	3.590 ± 0.048	1.3

[a] Corrected for Ce^{III} generated during the flash (see Experimental Section).

control the relative abundances of different Ce^{III} species. Then, in order to relate changes in k_{II} to changes in the relative abundances of different Ce^{III} species, we assumed that the NO_3 free radical must act as a "kinetic microprobe" of these different Ce^{III} structures present, reacting with each species at a different specific rate (a process we have termed *competitive electron transfer*). If this interpretation was correct, it should be possible to obtain direct information about the concentration distribution of each Ce^{III} species. However, to accomplish this objective it would be necessary to define the several formation constants so they would be independent of ionic strength upon changing solvent composition. Thus, we required an unambiguous set of formation constants defined strictly by thermodynamic activity.

It is generally considered that $HONO_2$ is only partially dissociated in aqueous solutions and may be represented by the chemical equilibrium

$$\mathrm{HONO_2} \rightleftharpoons \mathrm{H^+} + \mathrm{NO_3^-} \qquad (1)$$

where the probability of a more complex ionization reaction involving the solvent is neglected. Accepting (1), we needed to know whether the variation in k_{II} depended on the stoichiometric concentrations of either H^+ or NO_3^-. To test the possible effect of $[H^+]$ on k_{II} at fixed $[NO_3^-]$, a series of flash kinetic studies was conducted, where the $(NH_4)_2Ce(NO_3)_6$ salt was dissolved in aqueous $HOClO_3$ solutions of different concentrations. $HOClO_3$ is believed to be the most suitable solvent system for such a test because: (1) the NO_3 free radical was identified by the flash spectroscopic technique in 5.50 M $HOClO_3$ solution (with no added $HONO_2$) and displayed no significant change in the solution absorption spectrum from that obtained in $HONO_2$; (2) $[H^+]$ was easily ascertained, since $HOClO_3$ may be assumed to be completely dissociated up to 8.0 M in aqueous solutions;[12] (3) the interfering complexation of ClO_4^- with Ce^{III} is known to be negligible in this medium up to an acid strength of 6.0 M.[13] Hence, using exactly the same pseudo-first-order kinetic method as with the $HONO_2$ solutions, the value of k_{II} was determined for $[HOClO_3]$ ranging from 1.52 to 5.59 M. Table II summarizes the results of this study and reveals that k_{II} is essentially unaffected by the change in $[H^+]$, with an average value of 0.355×10^6 M^{-1} sec^{-1}. Unfortunately, a similar test of the dependence of k_{II} on $[NO_3^-]$ at fixed $[H^+]$ is not possible, being limited both by salt solubility and the hydrolysis of the cerium salts. The acid strength must be maintained sufficiently high (≥ 1.0 M) to avoid hydrolysis, but at these high ionic strengths $[NO_3^-]$ becomes ill defined.

In view of the fact that the bimolecular rate constant k_{II} is independent of $[H^+]$, the description of the solvent system was again considered in terms of eq 1. The equilibrium constant for this expression (at a specific temperature) is described by the thermodynamic relation

$$K_{\mathrm{HONO_2}} = \frac{a_+a_-}{a_\mathrm{u}}$$

where a_+ and a_- refer to the ionic activities of H^+ and NO_3^-, respectively, and a_u is the activity of the undissociated acid. However, the uncertainty involved in speaking of the individual ionic activities at finite concentrations limits experimental information to be framed in terms of the geometric mean of the two ionic activities, $a_\pm = (a_+a_-)^{1/2}$. Thus, to avoid any uncertainty which might arise from the use of mean ionic activities and to place all changes in solvent composition on the same operationally defined basis, the activity of undissociated $HONO_2$ (a_u) was selected as the most suitable parameter against which changes in k_{II} might be correlated with all changes in solvent composition.

2. Development of the Theoretical–Chemical Model. The experimental values of $k_{II} \pm \sigma$ given in Table I are displayed *vs.* the known values of a_u in the region b to c of Figure 1. The values for a_u at 25° were determined from a comprehensive collection of activity data compiled by Davis and DeBruin.[14]

To explain the fundamental behavior suggested by the correlation of k_{II} with a_u in terms of *competitive electron transfer*, a theoretical–chemical model was

[12] K. Heinzinger and R. E. Weston, Jr., *J. Chem. Phys.*, **42**, 272 (1965).

[13] G. R. Choppin and R. H. Dinius, *Inorg. Chem.*, **1**, 140 (1962).

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

Table II. Summary of Pseudo-First-Order Data in Aqueous $HOClO_3$ Solutions at 25 ± 1°

Initial sample composition			Observed rate data			
$[H^+]$,[a] M	$[Ce^{IV}] \times 10^3$ M	$[Ce^{III}]_A \times 10^3$ M	Half-life, μsec	$k' \times 10^{-3}$ sec^{-1}	$k_{II} \pm \sigma^b \times 10^{-6}$ M^{-1} sec^{-1}	$\pm\sigma$, %
1.52	2.51	10.02	184	3.76	0.373 ± 0.018	4.8
2.03	2.03	7.94	263	2.64	0.327 ± 0.017	5.2
2.50	2.08	8.05	263	2.64	0.324 ± 0.008	2.5
3.04	1.01	3.98	468	1.48	0.364 ± 0.009	2.5
3.51	1.01	4.10	453	1.53	0.366 ± 0.015	4.1
3.99	1.01	4.04	420	1.65	0.394 ± 0.020	5.1
4.56	1.00	4.04	495	1.40	0.334 ± 0.008	2.4
5.08	0.99	4.04	468	1.48	0.343 ± 0.006	1.8
5.59	1.03	4.07	420	1.65	0.372 ± 0.007	1.9
					Av 0.355 ± 0.013	

[a] Presumes $[H^+] = [HOClO_3]$. [b] Corrected for Ce^{III} generated during the flash (see Experimental Section).

derived based on three *a priori* assumptions. (1) The activity coefficients (γ_i) assigned to each Ce^{III} complex (C_i) can be neglected because they are either equal to each other or are unity in the low concentration range used in this study. (2) A specific rate constant (k_i), invariant over the entire a_u range, can be assigned to each different Ce^{III} complex (C_i). (3) The observed value of k_{II} at each a_u may be expressed as a sum of the specific rate constants (k_i), provided each species is weighted by its fractional contribution (λ_i) to the total $[Ce^{III}]$; *i.e.*

$$k_{II} = \sum_i \lambda_i k_i$$

The justification of these assumptions is chiefly proved by the satisfactory application and interpretation of the theoretical–chemical model to be presented. However, some comments ahead of the data should be made. With regard to the first assumption, Rossotti and Rossotti[15] have considered in detail the implications of activity coefficients in the determination of thermodynamic formation constants for complexes in solution. As these authors state, the required activity coefficients are seldom available and are often guessed. In the present study, with solutions having ionic strengths >1 M, guesses about activity coefficients are accepted with less confidence. For this reason, our first assumption is clearly stated. We realize it is not based on established theory nor on prior experimental evidence. Rather it is founded on our intuitive notion that if the method of *competitive electron transfer* (or any other experimental method) can distinguish between different species of ion complexes stoichiometrically, then both our first assumption and eq 2 below must be inherently true. If so, the other assumptions are reasonable since only a_u needs to be specified to define the thermodynamic equilibria involved.

Combining these *a priori* assumptions into a general theoretical–chemical model, we require only that the several Ce^{III} species rapidly establish chemical equilibria of the following stoichiometric form

$$C_i + a_u \overset{K_i}{\rightleftharpoons} C_{i+1}$$

The various formation constants, K_i, are first defined in terms of activities of the Ce^{III} complexes and of the undissociated $HONO_2$ in the usual way, but in accord with the first assumption, the fundamental mass action expression by this model becomes

$$K_i = \frac{[C_{i+1}]}{[C_i]a_u} \qquad (2)$$

One may then write the fraction of the total $[Ce^{III}]$ existing in any one complex species as

$$\lambda_i = \frac{[C_i]}{\sum_{i=1}^{n}[C_i]} \qquad (3)$$

such that $\Sigma_{i=1}{}^n\lambda_i = 1$, where n is the total number of different Ce^{III} complexes considered. The second assumption specifies that each C_i complex possess a specific bimolecular rate constant k_i, such that the value for k_{II} at any given value of a_u might be calculated in accord with the third assumption: *viz.*

$$k_{II}^* = \sum_{i=1}^{n}\lambda_i k_i \qquad (4)$$

The superscript is employed here to differentiate between the calculated (k_{II}^*) and measured (k_{II}) values of the bimolecular rate constant for process II.

Applying this model to the 17 experimental values of k_{II} presented in Table I, it was found that four complexes were the minimum number of Ce^{III} species necessary to fit the major features of the data curve displayed in Figure 1. Assuming then a "four complex" model and using substitutions based on eq 2 and 3, eq 4 becomes

$$k_{II}^* = \frac{k_1 + k_2K_1a_u + k_3K_1K_2a_u^2 + k_4K_1K_2K_3a_u^3}{1 + K_1a_u + K_1K_2a_u^2 + K_1K_2K_3a_u^3} \qquad (5)$$

The value of k_1 was selected as the specific bimolecular rate constant for complex C_1. This was first taken as the measured value of k_{II} in $HOClO_3$ solutions (see Table II). The value assigned to k_1 is displayed as the "$HOClO_3$ limit" for k_{II} in Figure 1, representing the minimum possible value for k_{II} measured in these kinetic studies. The values of k_2, k_3, k_4, K_1, K_2, and K_3 were obtained by program II (see Experimental Section) to give the best fit of k_{II}^* to the experimental values of k_{II} at each known value of a_u. The best computed values for these quantities are listed in Table III. Upon substitution into eq 5 and by using known values

---

(15) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961, Chapter 2.

Table III. Derived Specific Rate Constants and Formation Constants Assuming "Four Ce^{III} Complexes"

Ce^{III} Complex (i)	$k_i \pm \sigma$, M^{-1} sec^{-1}	$K_i \pm \sigma$
1	$(0.355 \pm 0.013) \times 10^6$ [a]	8.08 ± 2.54
2	$(1.13 \pm 0.06) \times 10^6$	$(1.91 \pm 0.26) \times 10^{-2}$
3	$(5.19 \pm 0.24) \times 10^6$	$[5 \times 10^{-4}]$ [b]
4	$[5 \times 10^2]$ [b]	

[a] Experimental lower limit for k_{II} as measured in $HOClO_3$ solutions (see Table II). [b] Insufficient data for an adequate evaluation of $\pm\sigma$.

for a_u, the solid curve in Figure 1 was calculated. The values of the measured (k_{II}) and calculated (k_{II}^*) bimolecular rate constants are compared at identical values of a_u in Table IV. Although the experimental values for k_{II} span only region b to c of Figure 1, the solid calculated curve which fits the data in that region was extended to cover the [$HONO_2$] range from 0.1 to 23.867 M (100% $HONO_2$). The values for k_{II} in region a to b of this curve were not determined because of uncertainties introduced by hydrolysis of the cerium salts at lower [$HONO_2$]. Although it is possible to maintain the acid strength by the use of properly proportioned $HONO_2$–$HOClO_3$ mixtures in this region, the values for a_u are not known for the mixed acid system. The pseudo-first-order analyses used for determining k_{II} are not suitable in region c to d of Figure 1, for it is found that Ce^{III} becomes increasingly oxidized to Ce^{IV} as [$HONO_2$] goes above 15 M.[8] This condition severely limited any quantitative investigation in this region.

Table IV. Comparison of Observed and Derived Second-Order Rate Constants for the "Four Complex" Model[a]

[$HONO_2$], M	log a_u[b]	$k_{II} \times 10^{-6}$ M^{-1} sec^{-1}	$k_{II}^* \times 10^{-6}$ M^{-1} sec^{-1}	Deviation, % k_{II}
1.00	−1.435	0.64	0.53	−17.2
2.00	−0.718	0.74	0.84	+13.5
2.50	−0.447	0.92	0.95	+3.3
3.00	−0.192	1.01	1.05	+4.0
3.50	0.038	1.11	1.13	+1.8
4.50	0.449	1.27	1.30	+2.4
5.00	0.632	1.44	1.41	−2.1
6.00	0.957	1.75	1.71	−2.3
6.50	1.106	1.98	1.91	−3.5
7.00	1.249	2.17	2.14	−1.4
7.50	1.380	2.41	2.39	−0.8
8.00	1.506	2.55	2.65	+3.9
10.00	1.961	3.61	3.61	0.0
12.00	2.360	4.07	4.09	+0.5
13.00	2.548	4.13	4.10	−0.7
14.00	2.740	3.98	3.94	−1.0
15.00	2.930	3.59	3.63	+1.1

[a] See Figure 1 for a plot of a_u *vs.* k_{II}^*. [b] Calculated from the activity data of Davis and DeBruin.[14]

In order to confirm that the transient species monitored at 635 nm for the kinetic measurements was the NO_3 free radical and that changes in acid produced no significant changes, the spectrum of NO_3 in 5.50 M $HOClO_3$ (with no added $HONO_2$) and in 2.0, 6.0, and 15.0 M $HONO_2$ was recorded photographically. The characteristic absorption maxima at 598, 635, and 671 nm in each case were essentially coincident with those previously established.[3] There was absolutely no evidence using either spectroscopic or kinetic techniques for the generation of NO_3 by the direct photolysis of $HONO_2$ as proposed elsewhere.[4]

3. Suggestion of Five Ce^{III} Complexes. Looking again at Table IV, the deviation of k_{II}^* from the corresponding experimental values for k_{II} remains within a ±4% limit except at 1.00 and 2.00 M $HONO_2$. Since each experimental value of k_{II} was precisely determined and the four complex model quite adequately fits the data for those points where [$HONO_2$] > 2.00 M, we believe the larger deviations of k_{II}^* indicate the presence of another formation equilibrium step in the region a to b of Figure 1. If so, our model must be extended to handle five Ce^{III} complexes. The broken line in Figure 1 shows the only change expected on converting the four complex model into a fully resolved "five complex" system.

In order to extend the theoretical–chemical model to include the possibility of a fifth Ce^{III} complex with minimum confusion in previous notation, we define that in the five complex model the first Ce^{III} complex be labeled C_0 and have a specific bimolecular rate constant k_0. Whence the first formation equilibrium is written as

$$C_0 + a_u \overset{K_0}{\rightleftharpoons} C_1 \tag{6}$$

where K_0 is the first formation constant. The four higher nitrate complexes are handled as indicated in deriving eq 2–5, except that the previous value assumed for k_1 must be changed. To be consistent with the five complex model, the $HOClO_3$ limit for k_{II} must now be defined in terms of the specific rate constant k_0, which represents C_0 in (6), and a new value of k_1 must be found such that $k_0 \leq k_1 \leq k_2$. This means that the value for K_1 previously calculated by the four complex model (henceforth referred to as "K_1") actually is the combination of the first two formation equilibria in the five complex model: *viz.*

$$C_0 + 2a_u \overset{\text{"}K_1\text{"}}{\rightleftharpoons} C_2$$

where "K_1" $= (K_0K_1)^{1/2} = ([C_2]/[C_0])^{1/2}(1/a_u)$.

Discussion

1. Comparison of Formation Constants. From recent solvent extraction studies[16,17] estimates of K_0 and K_1 are known to compare with our value of "K_1" obtained by *competitive electron transfer*. In the work conducted by Choppin and Strazik[17] solutions of $HONO_2$ in $HOClO_3$ at a fixed ionic strength of 1.0 were used for extraction studies. Upon increasing [NO_3^-] from 0 to 1.0 M, they interpreted their results in terms of two competing ionic equilibria

$$Ce^{3+} + NO_3^- \overset{K_0^{cs}}{\rightleftharpoons} CeNO_3^{2+} \tag{7}$$

$$CeNO_3^{2-} + NO_3^- \overset{K_1^{cs}}{\rightleftharpoons} Ce(NO_3)_2^{+} \tag{8}$$

where waters of hydration are omitted in the stoichiometry. At 25° their value $K_0^{cs} = 1.62 \pm 0.10$ was determined rather precisely but their second constant was only roughly estimated as $K_1^{cs} = 0.3$ to 0.6. In

---

(16) D. F. Peppard, G. W. Mason, and I. Hucher, *J. Inorg. Nucl. Chem.*, 24, 881 (1962).

(17) G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, 4, 1250 (1965).

obtaining these data they assumed that activity coefficients do not change as the ionic composition is varied at constant ionic strength.

To compare formation constants derived by *competitive electron transfer* with those from solvent extraction, it is necessary to relate them in terms of the same activity reference function, ξ. Writing $K_i = [C_{i+1}]/[C_i]\xi$ by analogy with eq 2, the K_i's obtained by our technique were determined for $[HONO_2] \geq 1.0$ *M* and for $\xi = a_u$. The values of K_0^{cs} and K_1^{cs} taken from Choppin and Strazik[17] were measured for $[HONO_2] \leq 1.0$ *M* and for $\xi = [NO_3^-] = [HONO_2]$. Using the equilibrium relation, $K_{HONO_2} = a_{\pm}^2/a_u = 15.4 \pm 2.1$,[14] and assuming $\xi = [HONO_2] \simeq a_{\pm}$ (good within ±10% when $[HONO_2] \leq 1.0$ *M*), we can compare with Choppin and Strazik by calculating our K_i's using the same reference function, $\xi = a_{\pm}$.

Since our formation constants K_0 and K_1 from the five complex model are analogous to K_0^{cs} and K_1^{cs} obtained from the solvent extraction study, then the quantity $(K_0^{cs}K_1^{cs})^{1/2}$ should agree with our value of "K_1" ($\xi = a_{\pm}$) from the four complex model. Taking $K_0^{cs} = 1.62 \pm 0.10$ and $K_1^{cs} = 0.45 \pm 0.15$, we find $(K_0^{cs}K_1^{cs})^{1/2} = 0.85 \pm 0.15$ as compared to "K_1" ($\xi = a_{\pm}$) $= 0.72 \pm 0.12$. This good agreement is strong evidence in favor of the five complex model and lends credence to the concept of *competitive electron transfer* as a novel approach for estimating and discovering formation constants defined precisely in terms of thermodynamic activity over an enormous concentration range. Unfortunately, similar data comparisons for our estimated values of K_2 and K_3 (see Table V) are not possible, because these constants were obtained in a concentration range hitherto inaccessible by other methods. Not too much can be presumed on the basis of this one example, but the results are encouraging and suggest that our method may be applicable to other free radicals and/or metal complex systems.

Table V. Comparison of Ce^{III} Nitrate Formation Constants at 25 ± 1°

$$K_i = \frac{[C_{i+1}]}{[C_i]\xi} \text{ and } K_{HONO_2} = \frac{a_{\pm}^2}{a_u} = 15.4 \pm 2.1^{14}$$

ξ	"K_1"	K_2	K_3
a_u	8.08 ± 2.54	$(1.91 \pm 0.26) \times 10^{-2}$	5×10^{-4}
$a_{\pm}$	0.72 ± 0.12	$(3.52 \pm 0.93) \times 10^{-2}$	6×10^{-3}

2. Nitrate Stoichiometry Compatible with Five Ce^{III} Complexes. Any realistic consideration of the composition and structure of the Ce^{III} complexes met with in this study must involve not only the association of NO_3^- ions with Ce^{III} but also the association of neutral solvent molecules such as H_2O and $HONO_2$. Furthermore, since care was taken to maintain the acid strength of solutions at a sufficient level (≥ 1.0 *M*) to minimize hydrolysis effects, one can justifiably eliminate the importance of hydrolyzed Ce^{III} species. Thus, it will be our primary purpose to distinguish the various Ce^{III} complexes by deducing from our evidence the exact number of nitrate-like ligands (either NO_3^- or $HONO_2$) which are associated with each species. We have no direct evidence bearing on the exact number of H_2O molecules associated with the ligand atmosphere of these Ce^{III} species.

Since each individual Ce^{III} complex is converted to a corresponding Ce^{IV} complex on oxidation by the NO_3 radical, and because our theoretical–chemical model presumed that each successive formation constant must involve the stepwise association of one additional nitrate anion with Ce^{III}, we should be able to write down a set of equations for all of the interrelated Ce^{III} and Ce^{IV} complexes in this system. However, before this set can be written, a suitable ion reference state must be selected which fixes either a lower or an upper limit on the number of nitrate groups to be associated with the ions in this set.

A possible lower limit is the "bare" hydrated Ce^{III} ion (*i.e.*, $Ce(H_2O)_n^{3+}$) having no associated nitrate ligands. In the present research, where NO_3 is interpreted to act as a kinetic microprobe of Ce^{III} complex structures, the initial sample solution necessarily contains sufficient nitrate ions such that an adequate fraction thereof are associated with the Ce^{IV} ion. This we know because the primary generation process (I) is always efficient. For the pseudo-first-order runs conducted in strong $HOClO_3$ solutions, the NO_3^- is at its lowest practical limit, $\simeq 10^{-3}$ *M*, but the generation of NO_3 reveals little about the exact state of nitrate complexation on either the Ce^{III} or Ce^{IV} species. For this reason, we let the complex C_0 represent the Ce^{III} species with the minimum degree of nitrate complexation without assuming it to be the bare hydrated ion.

Assigning an upper limit reference state is much more satisfactory. Ion migration studies[18] in 6.0 *M* $HONO_2$ have shown that the Ce^{IV} species move to the anode. Furthermore, complementary solvent extraction[19] and spectrophotometric[19,20] work in solutions where $[HONO_2] \geq 6.0$ *M* has indicated that $Ce(NO_3)_6^{2-}$ is not only the most likely anionic species responsible for the observed migration, but it appears to be the only stable Ce^{IV} complex under these conditions. Radial distribution curves[21] obtained from X-ray diffraction experiments on saturated aqueous solutions of $(NH_4)_2Ce(NO_3)_6$ indicate that 12 oxygen atoms are coordinated to the central Ce^{IV} cation to form the $Ce(NO_3)_6^{2-}$ complex ion. The six nitrate ions are interpreted to form bidentate linkages which give a Ce^{IV}-centered regular icosahedron. This suggested bidentate structure is further supported by a recent single-crystal X-ray diffraction investigation of $(NH_4)_2Ce(NO_3)_6$.[22] In accord with these various results, it appears that the highly positive Ce^{IV} ion displays a maximum coordination number of 12, which is satisfied by an upper limit of six bidentate nitrate ligands. Similar information for the maximum nitrate coordination of Ce^{III} is not so readily available; however, coordination numbers as high as 9[23] have been suggested for this ion in solution and as high as 12 from single-crystal X-ray diffraction data for $Ce_2Mg_3(NO_3)_{12} \cdot H_2O$.[24] Since Ce^{III} and Ce^{IV} both appear to attract the nitrate

---

(18) D. M. Yost, H. Russel, Jr., and C. S. Garner, "The Rare Earth Elements and Their Compounds," Wiley, New York, N. Y., 1947, p 61.

(19) A. W. Wylie, *J. Chem. Soc.*, 1474 (1951).

(20) A. Henshall, Ph.D. Thesis, Vanderbilt University, 1963.

(21) R. D. Larsen and G. H. Brown, *J. Phys. Chem.*, **68**, 3060 (1964).

(22) T. A. Beineke and J. Delguadio, *Inorg. Chem.*, 7, 715 (1968).

(23) T. Moeller, "The Chemistry of the Lanthanides," Reinhold, New York, N. Y., 1963, pp 53–61.

(24) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963).

ligands only by overall electrostatic forces,[17,23] we may predict a general decrease in complex ion formation upon going from Ce^{IV} to Ce^{III} solution systems. For this reason, we anticipated that the maximum number of nitrates associated with Ce^{III} in the present solution study would be five and, as shown below, this is substantiated by the five complex model.

Assuming that $Ce(NO_3)_6{}^{2-}$ is the highest nitrate complex of Ce^{IV}, the *competitive electron transfer* technique has revealed the following set of interrelated transitions

$$\begin{array}{lcll}
Ce^{III}\text{ species} & & Ce^{IV}\text{ species} & \\
C_0 \text{ or } CeNO_3{}^{2+} & + NO_3 \xrightarrow{k_0} & Ce(NO_3)_2{}^{2+} & \text{(IIa)} \\
C_1 \text{ or } Ce(NO_3)_2{}^{+} & + NO_3 \xrightarrow{k_1} & Ce(NO_3)_3{}^{+} & \text{(IIb)} \\
C_2 \text{ or } Ce(NO_3)_3 & + NO_3 \xrightarrow{k_2} & Ce(NO_3)_4 & \text{(IIc)} \\
C_3 \text{ or } Ce(NO_3)_4{}^{-} & + NO_3 \xrightarrow{k_3} & Ce(NO_3)_5{}^{-} & \text{(IId)} \\
C_4 \text{ or } Ce(NO_3)_5{}^{2-} & + NO_3 \xrightarrow{k_4} & Ce(NO_3)_6{}^{2-} & \text{(IIe)}
\end{array}$$

where the C_i's and k_i's from our five complex model are given explicit meaning. This is in obvious disagreement with the earlier assumption of Choppin and Strazik,[17] where the C_0 reference state was presumed to be the uncomplexed or bare hydrated Ce^{III} ion. However, the correlation of $K_0{}^{cs}$ and $K_1{}^{cs}$ from their solvent extraction study with K_0 and K_1 in our five complex model strongly suggests that we are each observing the same equilibria but differ according to which ion reference state is correct.

We believe that the $CeNO_3{}^{2+}$ ion is the most likely candidate for the C_0 species. Not only is it consistent with our results but it also makes sense from the fact that the minimum $[NO_3{}^-]$ is always in large excess of the $[Ce^{III}]$ and because $NO_3{}^-$ is a better complexing agent than $ClO_4{}^-$. If the bare hydrated ion reference state is correct, it would imply that a Ce^{III} nitrate complex ion higher than $Ce(NO_3)_5{}^{2-}$ remains unresolved by our new method and we think this is very unlikely from the known structural data cited above.

Another argument for our assignment of the C_0 complex comes from an analysis of the solvent extraction data which depends on the use of sensibly immiscible aqueous and organic liquid phases, in which Ce^{3+} is extractable but $Ce(NO_3)_m{}^{(3-m)+}$ is nonextractable from the aqueous to the organic phase. The extractant used by Choppin and Strazik was dinonylnaphthalenesulfonic acid (which they refer to as HD) dissolved in *n*-heptane. It was established that $NO_3{}^-$ was absent in the Ce^{3+} extracted by HD, and that the extraction process was described by the equation[17,25]

$$Ce_A{}^{3+} + [(HD)_x]_O \rightleftharpoons Ce(H_{x-3}D_x)_O + 3H_A{}^+$$

where A and O refer to the aqueous and organic phases, respectively. Assuming the equilibria expressed by eq 7 and 8, the observed changes in the distribution ratio of Ce^{III} between aqueous and organic phases as a function of $[NO_3{}^-]$ were used to determine $K_0{}^{cs}$ and estimate $K_1{}^{cs}$. We have presented evidence which reassigns (7) and (8) to become reactions 9 and 10, respectively.

$$CeNO_3{}^{2+} + NO_3{}^- \underset{}{\overset{K_0}{\rightleftharpoons}} Ce(NO_3)_2{}^+ \qquad (9)$$

$$Ce(NO_3)_2{}^+ + NO_3{}^- \underset{}{\overset{K_1}{\rightleftharpoons}} Ce(NO_3)_3 \qquad (10)$$

This change in interpretation does not alter the experimental results because it is still possible for the $NO_3{}^-$ associated with C_0 to be easily displaced by complexation with the extractant HD without affecting the reported values of $K_0{}^{cs}$ and $K_1{}^{cs}$. However, this change can explain why the attempted correlation between the log of the first stability constant and the ionic conductance of the bare M^{3+} ion (see Figure 2 of Choppin and Strazik[17]) failed only in the case of Ce^{III} but not for the other lanthanide nitrates because cerous nitrate dissolved in aqueous perchloric acid ≥ 1 *M* does not form the bare hydrated ion reference state but retains, as we contend, at least one nitrate ligand.

3. Steric Implications from Competitive Electron Transfer. An initial objective of this investigation was to deduce if possible the structural origins of the empirical steric factors, p_1 and p_2, described in the introduction. The p_2 factor was totally associated with the influence of $[HONO_2]$ on the value of k_{II} and the variations in k_{II} were interpreted by our theoretical–chemical model to be connected to the participation of five different Ce^{III} nitrate complexes. The five complex model was able to fit known formation constants. Hence, we concluded that the $HONO_2$ activity (a_u) controls the relative concentrations of the various Ce^{III} complexes, each of which competes in the consumption of NO_3 at a fixed specific rate. From eq 4 the relative mole fraction (λ_i) for each of the Ce^{III} complexes at any a_u can be determined from the formation constants derived from this model. Thus, it is clear that the "p_2 steric effect" is intimately related to the multiple formation equilibria and is specifically identified by the λ_i terms. Furthermore, if each k_i is now written in the form of a simple collision theory expression, eq 4 becomes

$$k_{II}{}^* = \sum_{i=1}^{5}\lambda_i k_i = \sum_{i=1}^{5}\lambda_i p_i z_i e^{(E_a)_i/RT} \qquad (11)$$

and we can quickly identify the p_i terms with what we first called the "p_1 steric effect." Since the p_i's are related to kinetic factors, whereas the λ_i's depend on chemical equilibria, the p_1 and p_2 effects would have been better labeled the "dynamic" and "static" steric effects, respectively. In addition, explanations for at least two dynamic structural problems are hidden in in p_i terms.

Problem 1. Explaining the Relative Magnitudes of the k_i's. Upon applying our five complex model to the data, we found that the specific rate constants possess the following sequence of relative magnitudes: $k_4 \ll k_0 < k_1 < k_2 < k_3$, where the value of k_1 is assumed to lie somewhere between k_0 and k_2. Hence, any chemical–structural interpretation attached to the p_i terms must provide an explanation for the fact that the values of k_i's increase for the first four complexes but the value of k_4 decreases sharply.

Each arbitrary p_i covers a multitude of possible structural difficulties regulating the ease by which an electron is transferred. Any attempt to delineate this problem must include what is known about the ligand configuration in the cerium nitrate complexes. In general, the cerium species owe their specific properties

---

(25) G. R. Choppin and P. J. Unrein, *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).

to the interaction between well-shielded 4f electrons in an inner valence shell with the outer ligand atmosphere. We also know that 4f electrons are so well shielded from the surrounding medium by overlapping 5s and 5p electrons that the resulting cerium coordination centers are effectively an inert-gas-type ion, attracting ligands only by overall electrostatic forces.[23] Present theories of ionic solutions contend that in dilute aqueous acid media the cerium ion is enclosed within a sheath (or "inner sphere") of polarized water molecules with which the nitrate ions must compete to occupy positions in the first coordination sphere.[17,23] Hence, there should be relatively weak ion-pair formation between cerium and the nitrate ligands. Although water apparently competes quite favorably with nitrate ions for positions in the first coordination sphere in dilute aqueous solution, X-ray diffraction[21] and infrared and Raman[26] studies on saturated aqueous solutions of $(NH_4)_2Ce(NO_3)_6$ have found little evidence for intervening hydration in the coordination of nitrate ions with Ce^{IV}. For the solutions used in the present study, one would expect that increasing nitrate complexation on Ce^{III} should involve increased displacement of water molecules from the inner hydration sphere in favor of the nitrate ligands.

The results of this study are in accord with the preceding ideas. Moreover, they provide a possible way to rationalize the trends of the k_i data by suggesting that the background solvent plays an active role in displacing water molecules from the first coordination sphere of Ce^{III}. For example in the $HOClO_3$ solutions, we showed that $CeNO_3^{2+}$ is the predominant species. Although there is some complexation between NO_3^- and Ce^{III}, hydration definitely predominates over anionic association. The central metal ion is effectively insulated from the NO_3 radical and the rate of process (II) is slow owing to the reduced probability of electron transfer through the predominant hydration layer. Upon increasing $[HONO_2]$, the increased nitrate concentration can compete more efficiently with water for coordination positions on Ce^{III} and, in effect, the background solvent assists in the displacement of water, producing a gradually increased probability of electron transfer such that $k_0 < k_1 < k_2 < k_3$, where each k_i has a low activation energy of 1–2 kcal/mol. However, above 13 *M* $HONO_2$, solvent assistance in the displacement of waters of hydration as expressed in the relative sizes of the p_i terms is overwhelmed by an abrupt increase in the activation energy barrier for the last transition

$$C_4 \text{ or } Ce(NO_3)_5^{2-} + NO_3 \xrightarrow{k_4} Ce(NO_3)_6^{2-}$$

This energy barrier cannot be measured reliably, since at 15 *M* only about 29% of the Ce^{III} complexes are in the C_4 state and we are unable to make kinetic measurements at elevated temperatures because of the competing spontaneous oxidation of Ce^{III} by $HONO_2$. We do estimate that $E_a \geq 6$ kcal/mol for the C_4 complex, and there is little doubt that this explains why k_4 is so small compared to the other k_i's. It should also come as no surprise that the formation of the most symmetrical icosahedral complex, $Ce(NO_3)_6^{2-}$, should involve an appreciable activation energy to help make up for the considerable entropy decrease and structural reorganization necessary to achieve this final state.

Problem 2. Explaining Why the Absolute k_i's Are So Far from a Diffusion-Controlled Limit. In considering the configuration of the NO_3^- (or $HONO_2$) ligands of the Ce^{III} and Ce^{IV} complexes, one finds a possible explanation for this problem which accounts for the low values we found of the order of 10^{-4}–10^{-5} for the dynamic, or p_i, steric factors. It is interesting that no studies of the Ce^{III} [27,28] and Ce^{IV} [21,26] nitrate complexes in aqueous solution have indicated any other than bidentate coordination for the NO_3^- (or $HONO_2$) ligands. Hence, it is reasonable to presume that the spontaneous electron transfer from Ce^{III} to the incoming NO_3 radical must ultimately take place *via* a transition state which is sterically very difficult to achieve because of this bidentate requirement. Another steric complication may be that the incoming NO_3 might have to force the displacement of one or possibly two water molecules from the inner coordination sphere before achieving the desired bidentate transition state. We have already mentioned that the solvent may assist these displacements. Such assistance may only be part of a more general participation of the solvent in helping the incoming NO_3 group to reorganize the entire ligand atmosphere before electron transfer is complete.

Although these steric arguments are admittedly qualitative, they are in accord with all known structural data on cerium nitrate complexes and provide a physical explanation as to why all of the k_i's we have deduced are so far from the diffusion-controlled limit, whereas only k_4 appears to be seriously energy limited.

---

[26] J. T. Miller and D. E. Irish, *Can. J. Chem.*, **45**, 147 (1967).

[27] R. E. Hestor and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

[28] J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nucl. Chem.*, **29**, 139 (1967).