Thermodynamic Quantities from Kinetic Measurements. Free Energy of Formation of the Nitrate Radical in Solution[1]

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Abstract: By an analysis of the restrictions resulting from the experimental observation of a simple order with respect to total concentrations for systems containing interconvertible complex ions, it is shown that either the rate of equilibration among species is fast or that each complex species reacts with the same specific rate constant. This result and published kinetic and thermodynamic data are used to place a lower limit of 21.6 kcal. on the Gibbs free energy of formation of the NO_3 radical in 6 *F* HNO_3 at 50°.

A study of the rate of the reaction[2]

$$NO_3 + Ce(III) \xrightarrow{k_1} Ce(IV) + NO_3^- \tag{1}$$

may be coupled with the results of an earlier study of the Tl(I)-Ce(IV) reaction[3] and other data to obtain an estimate of the free energy of formation of the NO_3 radical in solution.

The first step of the Tl(I)-Ce(IV) reaction was postulated to be

$$Ce(IV) + NO_3^- \xrightarrow{k_2} Ce(III) + NO_3 \tag{2}$$

or

$$Ce(IV) + OH^- \longrightarrow Ce(III) + OH \tag{3}$$

where the symbols do not imply the detailed nature of the ions. Indeed Ce(IV) exists as complex ions, and probably the reactive NO_3^- or OH^- (or H_2O) is incorporated in the complex species before reaction. Because of the agreement of ratios of rate constants in widely differing media, Dorfman and Gryder were "tempted to conclude. . .that OH rather than NO_3 is the kinetic intermediate." However, the flash photolysis results of Martin, *et al.*,[2,4] almost certainly indicate that NO_3 is the intermediate. We shall assume this to be the case.

The experimental papers defined pseudo rate constants which are valid at sufficiently high constant concentrations of NO_3^- and H^+ and at sufficiently low concentrations of cerium to permit the assumption of constant activity coefficients and the neglect of polymer formation. These constants are given by

$$-\frac{dC_3}{C_3(NO_3)dt} = k_1 \tag{4}$$

and

$$-\frac{dC_4}{C_4dt} = k_2 \tag{5}$$

where C_3 and C_4 are the total concentration of Ce(III) and Ce(IV), respectively.

A more detailed consideration of the complex nature of the system yields greater insight into the physical significance of these pseudo constants. The Ce(IV) ion exists as various complexes, $Ce(NO_3)_i(OH)_j^{4-i-j}$, each of which may react to yield initially various Ce(III) complexes, $Ce(NO_3)_r(OH)_s^{3-r-s}$. The Ce(IV) species with *i* nitrate and *j* hydroxide ligands will be labeled C_{4ij}, and the Ce(III) species with *r* nitrate and *s* hydroxide ligands will be labeled C_{3rs}. Reactions 1 and 2 will consist of one or more concurrent steps. Representative examples of these steps are

$$C_{4ij} \rightleftarrows C_{3rs} + NO_3 + (i - r - 1)NO_3^- + (j - s)OH^- \tag{6a}$$

$$C_{4ij} + (r + 1 - i)NO_3^- \rightleftarrows C_{3rs} + NO_3 + (j - s)OH^- \tag{6b}$$

$$C_{4ij} + (j - s)H^+ \rightleftarrows C_{3rs} + NO_3 + (i - r - 1)NO_3^- + (j - s)\, H_2O \tag{6c}$$

$$C_{4ij} + (s - j)OH^- \rightleftarrows C_{3rs} + NO_3 + (i - r - 1)NO_3^- \tag{6d}$$

The experiments were performed using a constant excess concentration of HNO_3; and, therefore, the general microstep can be written, after simplifying the notation, as

$$C_{4i} \rightleftarrows C_{3r} + NO_3 \tag{7}$$

where *i* and *r* now represent species with a specified number of NO_3^- *and* OH^- ligands. The pseudo microconstants for the forward and reverse directions of reaction 7 will be symbolized as k_{4i3r} and k_{3r4i}, respectively. These constants are the sums of the constants, including (H^+) and (NO_3^-) dependence, for appropriate members of reactions 6. The rate at which one cerium complex is converted into another must also be considered. The specific rate constants, including acid and nitrate dependence for the reaction $C_{4i} \rightarrow C_{4j}$, will be labeled α_{4ij} and α_{3rs} for the analogous Ce(III) species. The rate expression for the change in C_{3r} under conditions such that the forward reaction of 7 can be ignored can now be written as

$$\frac{dC_{3r}}{dt} = -\sum_i k_{3r4i}(NO_3)C_{3r} - \sum_{s \neq r} \alpha_{3rs}C_{3r} + \sum_{s \neq r} \alpha_{3sr}C_{3s}$$

By dropping the subscript 3 and defining k_r as $\sum_i k_{3r4i}$, the equation is simplified to

$$\frac{dC_r}{dt} = -k_r(NO_3)C_r - \sum_{s \neq r} \alpha_{rs}C_r + \sum_{s \neq r} \alpha_{sr}C_s \tag{8}$$

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[2] T. W. Martin, R. E. Rummel, and R. C. Gross, *J. Am. Chem. Soc.*, **86**, 2595 (1964).

[3] M. K. Dorfman and J. W. Gryder, *Inorg. Chem.*, **1**, 799 (1962).

[4] T. W. Martin, A. Henshall, and R. C. Gross, *J. Am. Chem. Soc.*, **85**, 113 (1963).

Return now to the experimental observation of eq. 4 and the fact that $C_3 = C_3(0) - (NO_3)_0 + (NO_3)$ where $C_3(0)$ and $(NO_3)_0$ are initial concentrations. We find

$$\frac{d(NO_3)}{dt} = -k_1(NO_3)[C_3(0) - (NO_3)_0 + (NO_3)] \quad (9)$$

and therefore (NO_3) is a known function of time. If this function of time is substituted into eq. 8, a system of linear differential equations is obtained which has a unique solution for given initial conditions.[5] We note, however, that the summation of eq. 8 over all r is equal to the total rate of change of C_3, and since the last two sums cancel after the additional summation over r, we obtain

$$\frac{dC_3}{dt} = -\sum_r k_r(NO_3)C_r$$

which when combined with eq. 4 after using the identity $\sum_r C_r = C_3$, yields

$$\sum_r k_rC_r = k_1C_3 \quad (10)$$

This result will not, in general, be compatible with the unique solution to eq. 8. Indeed only certain values of the rate constants will simultaneously satisfy eq. 8, 9, and 10. In order to simplify the presentation, we shall use as the boundary condition that initially all the cerous complexes are in equilibrium. Therefore

$$\sum_{s\neq r}\alpha_{rs}C_r(0) = \sum_{s\neq r}\alpha_{sr}C_s(0) \quad (11)$$

We now look for a power series solution

$$C_r(t) = C_r(0) + \left(\frac{dC_r}{dt}\right)_{t=0} t + \frac{1}{2}\left(\frac{d^2C_r}{dt^2}\right)_{t=0} t^2 + \dots$$

Define γ_r such that $k_r = k_1 + \gamma_r$ and obtain with the aid of eq. 10

$$\Sigma\gamma_rC_r = 0 \quad (12)$$

This equation must be true for all time and, therefore, when the series solution is substituted into eq. 12, the coefficient of each power of time is zero. Hence

$$\sum_r \gamma_rC_r(0) = 0, \sum_r \gamma_r\left(\frac{dC_r}{dt}\right)_{t=0} = 0, \text{etc.} \quad (13)$$

The first of these equations is seen to be true from eq. 12. From eq. 8 and 11 we obtain

$$\left(\frac{dC_r}{dt}\right)_{t=0} = -(k_1 + \gamma_r)[C_r(0)](NO_3)_0$$

and from this result and eq. 13 find

$$\sum\gamma_r\left(\frac{dC_r}{dt}\right)_{t=0} = -k_1(NO_3)_0\sum\gamma_rC_r(0) - (NO_3)_0\sum\gamma_r^2C_r(0) = 0$$

The first of these sums is zero from eq. 12, and since C_r must be positive, the second sum can be zero only if all the γ_r's are zero. Thus the only solution compatible with eq. 8, 9, and 10, and the boundary condition is that each k_r is equal to k_1. The argument can be generalized to include other boundary conditions.

It is unlikely that the k_r's are all equal. The more reasonable assumption is that the rate of equilibration between species is fast in comparison with the rate of reaction between cerium and NO_3 radicals and that eq. 4 is only approximately correct. This result is easily generalized, and we conclude that whenever an empirical rate expression has simple dependence on total concentration of reactants in a complex system, rapid equilibrium between species is probable.

Returning now to the more complex symbolism of eq. 6 and assuming that the rate of equilibration is fast, we find

$$C_3 = \sum_{r,s}C_{3rs} = \sum_{r,s}\beta_{rs}(Ce^{+3})(NO_3^-)^r(OH^-)^s \quad (14)$$

where (Ce^{+3}) is the concentration of uncomplexed Ce(III), β_{rs} is the association constant for the species C_{3rs}, and β_{00} is 1. Hence

$$\frac{C_{3rs}}{C_3} = \frac{\beta_{rs}(NO_3^-)^r(OH^-)^s}{\sum_{r,s}\beta_{rs}(NO_3^-)^r(OH^-)^s} \quad (15)$$

Since, by assumption, equilibrium is maintained and since (NO_3^-) and (H^+) are essentially constant under the experimental conditions, the derivative of eq. 15 with respect to time is zero. Hence

$$\frac{dC_{3rs}}{C_{3rs}dt} = \frac{dC_3}{C_3dt} = -k_1(NO_3)$$

and k_1 is seen to describe not only the rate of disappearance of total Ce(III) but also of each species.

If the mechanism of the forward and reverse reactions determined under the experimental conditions remains valid as equilibrium is approached, a pseudo equilibrium constant is obtained from eq. 4 and 5.

$$\frac{k_2}{k_1} = \frac{C_3(NO_3)}{C_4}$$

Then from eq. 14 and a similar one for Ce(IV) we obtain

$$\frac{C_3(NO_3)}{C_4(NO_3^-)} = \frac{k_2}{k_1(NO_3^-)} = \frac{(Ce^{+3})(NO_3)\sum_{r,s}\beta_{rs}(NO_3^-)^r(OH^-)^s}{(Ce^{+4})(NO_3^-)\sum_{ij}\xi_{ij}(NO_3^-)^i(OH^-)^j} \quad (16)$$

where ξ_{ij} are the association constants for the species C_{4ij} and $\xi_{00} = 1$. Note also that the factor $(Ce^{+3})\cdot(NO_3)/[(Ce^{+4})(NO_3^-)]$ is just the equilibrium constant for uncomplexed species in the reaction $Ce^{+4} + NO_3^- = Ce^{+3} + NO_3$.

Consider now the reaction

$$Ce(IV) + {}^1/{}_2H_2(g) = Ce(III) + H^+$$

A pseudo equilibrium constant for this reaction is defined as

$$\frac{C_3(H^+)}{C_4P_{H_2}^{1/2}} = K\frac{\sum_{r,s}\beta_{rs}(NO_3^-)^r(OH^-)^s}{\sum_{ij}\xi_{ij}(NO_3^-)^i(OH^-)^j} = K_a \quad (17)$$

where K is the equilibrium constant for the reaction involving uncomplexed cerium and K_a is the pseudo

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(5) See, for example, L. R. Ford, "Differential Equations," McGraw-Hill Book Co., Inc., New York, N. Y., 1933, p. 95.

constant using total concentrations. The ratio of eq. 16 to 17 yields

$$\frac{(NO_3)P_{H_2}^{1/2}}{(H^+)(NO_3^-)} = \frac{k_2}{k_1(NO_3^-)K_a} \qquad (18)$$

which is the equilibrium constant for the reaction

$$H^+ + NO_3^- = NO_3 + {}^1/_2H_2(g) \qquad (19)$$

All of the quantities on the right of eq. 18 are known or can be estimated at 50°. From ref. 2 we calculate $k_1 = 1.96 \times 10^6$, and from ref. 3 we find $k_2 = 1.33 \times 10^{-5}$. The value of K_a can be calculated from the formal potential, measured at 50°, of the Ce(III)–Ce(IV) half-cell in 6 F HNO_3 relative to the standard hydrogen half-cell. This latter value is not known with certainty. However, the work of Noyes and Garner[6] indicates that the variation of this potential with temperature is less than 0.01 v. when temperature is changed from 0 to 25° for a medium consisting of 1 F HNO_3 and 1 F $HClO_4$. This observation, coupled with the measurements of Smith,[7] leads us to estimate the formal potential of 6 F HNO_3 at 50° to be 1.59 ± 0.02 v. The value of K_a is then found to be 6.6×10^{24}, and the value of the equilibrium constant for reaction 19 is 1.7×10^{-37}. This value yields a free energy of reaction of 54.4 kcal. and an $E°$ for the half-reaction $NO_3^- = NO_3 + e^-$ of −2.35 v. at 50°. Finally, with the aid of the free energy of formation[8] of aqueous HNO_3, calculated to be −32.79 kcal. at 50°, we obtain the free energy of formation of aqueous NO_3 radical at 50° to be 21.6 kcal.

Our numerical results are, of course, based on the assumption that the intermediate in the Ce(IV)–Tl(I) reaction is NO_3. If the intermediate is actually OH, we would conclude that the thermal rate of formation of NO_3 is less than that for OH and therefore the equilibrium constant in eq. 18 would be smaller than that calculated above, giving a larger value for the free energy of reaction 19 and a larger value for the free energy of formation of aqueous NO_3. Our value of 21.6 kcal. is therefore seen to be a lower limit. Independent evaluations of this quantity are underway.

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Crystal and Molecular Structure of Bis(N-isopropylsalicylaldiminato)copper(II)

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Abstract: The crystal structure of bis(N-isopropylsalicylaldiminato)copper(II), $(C_3H_7N{=}CHC_6H_4O)_2Cu$, has been determined by X-ray diffraction analysis. The crystals are orthorombic, space group Pbca. Cell dimensions are $a = 12.87 \pm 0.04$, $b = 20.68 \pm 0.03$, $c = 14.58 \pm 0.03$ Å.; $Z = 8$. The coordination around the copper atom is a flattened tetrahedron with symmetry C_2. The angle between the planes defined by the Cu–N-1–O-1 and Cu–N-2–O-2 groups is about 60°.

It has been reported[1] that bis(N-isopropylsalicylaldiminato)copper(II), $(C_3H_7N{=}CHC_6H_4O)_2Cu$, is nearly, but not perfectly isomorphous with the analogous nickel complex, which was shown to be tetrahedral by means of magnetic, spectrophotometric, and molecular weight measurements.[2] A recent three-dimensional X-ray analysis[3] has confirmed the nickel complex to have a tetrahedral structure, although slightly distorted.

It is concluded that the copper atom has in bis(N-isopropylsalicylaldiminato)copper(II) a similar, but somewhat distorted, configuration.

It has been independently reported[4] that copper complexes with N-alkylsalicylaldimines can occur in tetrahedral or planar configurations, depending on the nature of the alkyl group and of the ring substituents, and that these structures can be recognized on the basis of their ultraviolet and visible spectra.[4a] Recently, the structure of bis(N-*t*-butylsalicylaldiminato)copper(II)[5] has been studied by X-ray analysis and found to be a distorted tetrahedron, as suggested on the basis of its reflectance spectrum.[4a]

In order to provide some precise information about the structure of bis(N-isopropylsalicylaldiminato)copper(II), we have undertaken a three-dimensional X-ray analysis.

Experimental Section

Bis(N-isopropylsalicylaldiminato)copper(II) was prepared by the reaction between bis(salicylaldehydato)copper(II) and isopropylamine in methanol.

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