coordinated to chromium(III). The failure of sulfate to act as a bidentate ligand with chromium(III) has been attributed to the fact that the O–O distance in sulfate is too small.[6,10] Finholt, *et al.*, have estimated that for bidentate attachment the O–O distance in a ligand should be about 2.78 A. The sulfate O–O distance is 2.34 A,[11] while for hypophosphite the O–O distance is 2.56 A.[12] One can speculate that hypophosphite is more likely than sulfate to act as a bidentate ligand because of its greater O–O distance. Infrared studies of hypophosphitochromium(III) might indicate whether the ligand is bidentate or monodentate.

Acknowledgments.—We wish to thank Dr. John Cooper and Dr. William Child for helpful discussions. We also wish to thank the National Science Foundation, Undergraduate Research Participation Program, for partial financial support of this work.

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A Kinetic Study of the Hexaaquoiron(III)–Hexacyanoferrate(III) Complex

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The mechanism for the complexation reaction between hexaaquoiron(III), $Fe(H_2O)_6{}^{3+}$, and hexacyanoferrate(III), $Fe(CN)_6{}^{3-}$, is

$$Fe(H_2O)_6{}^{3+} + Fe(CN)_6{}^{3-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Fe(H_2O)_6Fe(CN)_6$$

$$Fe(H_2O)_6Fe(CN)_6 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Fe(H_2O)_5Fe(CN)_6 + H_2O$$

where $Fe(H_2O)_6Fe(CN)_6$ is an ion pair and $Fe(H_2O)_5Fe(CN)_6$ is the complex. The equilibrium concentration quotient for the first reaction above is K. At 298°K $k_{32} = 15.0 \pm 1.0$ sec^{-1} and $k_{23}K = 1750 \pm 250$ M^{-1} sec^{-1}. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_{32} are 8.8 ± 0.6 kcal/mole and 5.5 ± 2.0 eu, and $\Delta H^{\ddagger}$ for $k_{23}K$ is 24.6 ± 1.6 kcal/mole. The rate constant k_{23} and K are estimated to be 50 sec^{-1} and 35 M^{-1} at 298°K. Comparisons of k_{23} are made with the water-exchange rate constant for hexaaquoiron(III) and rate constants for the formation of other iron(III) complexes.

Introduction

The equilibrium properties of the aqueous hexaaquoiron(III)–hexacyanoferrate(III) [$Fe(H_2O)_6{}^{2+}$–$Fe(CN)_6{}^{3-}$] system have been studied in some detail by Ibers and Davidson.[1] The concentration quotient for the reaction

$$Fe(H_2O)_6{}^{3+} + Fe(CN)_6{}^{3-} = Fe(H_2O)_5Fe(CN)_6 + H_2O \quad (1)$$

has been determined under a variety of conditions. This work reports a kinetic study of reaction 1 by temperature-jump relaxation techniques. The kinetic results are correlated with the rate constant for water exchange of hexaaquoiron(III) and rate constants for the formation of other iron(III) complexes.

Experimental Section

Chemicals.—Hydrated iron(III) perchlorate was prepared by evaporation of a solution of hydrated iron(III) chloride (Mallinckrodt, analytical reagent) in 70% perchloric acid. Sodium perchlorate was prepared by boiling sodium carbonate (Baker, reagent) in a perchloric acid solution to dryness. Potassium hexacyanoferrate(III) (Mallinckrodt, reagent) was used without additional purification. The potassium ion concentration was sufficiently small so that potassium perchlorate did not precipitate. Sodium hexacyanoferrate(III) which had been recrystallized from water–ethanol mixtures was used in experiments where excess hexacyanoferrate(III) was required.

Solutions.—Deionized water was used in the preparation of all solutions. The concentration of iron(III) in stock iron(III) perchlorate solutions was determined by first reducing iron(III) to iron(II) with a Jones reductor followed by titration with dichromate using diphenylamine as an indicator.[2] The iron(III) perchlorate solutions were made up in 1.0 or 0.5 M perchloric acid to prevent hydrolysis. Hexacyanoferrate(III) solutions were analyzed by measurement of the absorbance at 420 mμ where ϵ is 1.1×10^3 M^{-1}.[1] The pH values of the solutions were measured with a Leeds and Northrup 7401 pH meter. The saturated KCl solution in the calomel electrode was replaced with a 4.0 M lithium chloride solution to prevent precipitation of potassium perchlorate. The pH meter was calibrated in the pH 0–1.0 range with standardized perchloric acid solutions at the same ionic strength as the solutions used in the experiments. The hydrogen ion concentration was accurate to ±0.02 M.

Apparatus.—The temperature-jump relaxation instrumentation was manufactured by the Messanlagen Studiengeschellschaft, G.m.b.H., Göttingen, Germany. The instrument was thermostated to ±0.5° and the change in visible spectrum was

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(1) J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **73**, 476 (1951).

(2) K. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 579.

used to monitor the relaxation. The conditions for using relaxation methods to evaluate the kinetics of a system are the following. First, the system must be at equilibrium. Second, when a perturbation is applied to the system to change the equilibrium (*e.g.*, temperature perturbation), the change must be small enough so that the rate equations can be linearized, that is, $\Delta G/RT \ll 1$. Then $\mathrm{d}c_i/\mathrm{d}t = -(c_i - \bar{c}_i)/\tau$, where c_i and $\bar{c}_i$ are concentrations of the ith species in the perturbed and the equilibrium state and τ is the relaxation time. Thus τ can be obtained from a plot of the logarithm of a quantity related to c_i *vs.* time, t. The relaxation time is related to the rate constants and concentrations of the species in the equilibrium state established after the perturbation in a unique way depending on the mechanism.[3] The temperature change of the system was 5°, and the minimum observable relaxation time was about 1 μsec.

All additional spectral measurements were made with a Cary Model 14 recording spectrophotometer with temperature control to ±0.5°.

Experiments.—Previously thermostated stock hexaaquoiron(III) and hexacyanoferrate(III) solutions were mixed just before introduction into the temperature-jump cell to minimize the decomposition of the solutions. Our experiments confirmed the observations of other workers concerning the slow acid decomposition of $Fe(CN)_6^{3-}$.[1] However, this decomposition did not interfere with the experiments. Temperature-jump relaxation experiments were carried out at 500 mμ. At this wavelength, the extinction coefficient of the complex is about 600 M^{-1} cm^{-1}, while the other species present do not absorb to any appreciable extent.[1] All temperature-jump experiments were carried out either in excess hexaaquoiron(III) or hexacyanoferrate(III) so that ($[Fe(CN)_6^{3-}] + [Fe(H_2O)_6^{3+}]$) could be approximated by $[Fe(H_2O)_6^{3+}]$ or $[Fe(CN)_6^{3-}]$. The recorded error in $\Delta H^{\ddagger}$ for the rate constants corresponds to one-fourth of the limits of uncertainty of the corresponding $\ln (k/T)$ *vs.* $1/T$ plots. This is a good measure of the probable error.[4] The error in $\Delta S^{\ddagger}$, $\delta\Delta S^{\ddagger}$, is taken as $\delta\Delta H^{\ddagger}/T$.

Results

Figure 1 contains plots of $1/\tau$ *vs.* ($[Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}]$) at various temperatures in 0.5 M $HClO_4$. Within experimental error the data are the same in 1.0 M $HClO_4$ solutions ($\blacktriangle^1$ points in Figure 1), in a solution containing 0.1 M La^{3+} and 0.5 M $HClO_4$ ($\blacktriangle^2$ point in Figure 1), and in solutions containing 0.5 M $HClO_4$ and 0.5 M $NaClO_4$ ($\blacktriangle^3$ points in Figure 1). Thus the deviation of the plots in Figure 1 from linearity is not ascribable to an ionic strength effect. Figure 2 contains a typical relaxation curve for the system. Point a corresponds to an absorbance of the solution before any temperature perturbation is applied. After the perturbation, there appear to be two substantial absorbance increases which do not occur under comparable conditions with hexaaquoiron(III) or hexacyanoferrate(III) solutions alone. The observed absorbance changes are unaltered when the experiments are carried out in 1.0 M $HClO_4$. Thus a hydrolysis reaction is not the source of any of the changes. One absorbance change is rapid and occurs under all experimental conditions in less than 1 μsec (a to b in Figure 2). The second absorbance change has a relaxation time in the millisecond range (b to c in Figure 2) and is the one plotted in Figure 1.

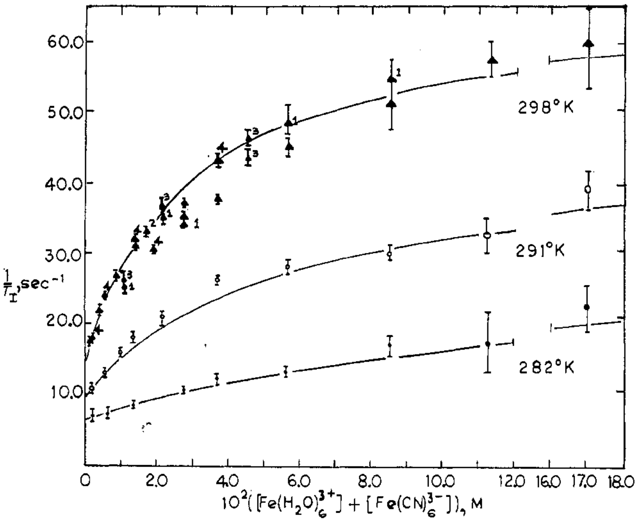

Figure 1.—Plot of $1/\tau_I$ *vs.* ($[Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}]$) at 298, 291, and 282°K. All experiments in 0.5 M $HClO_4$ except those marked by $\blacktriangle^1$ (1.0 M $HClO_4$), $\blacktriangle^2$ (0.1 M La^{3+} and 0.5 M $HClO_4$), $\blacktriangle^3$ (0.5 M $HClO_4$ and 0.5 M $NaClO_4$), and $\blacktriangle^4$ (excess $Fe(CN)_6^{3-}$).

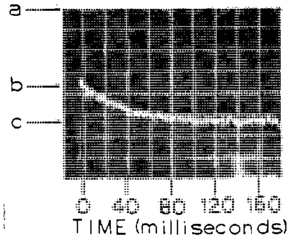

Figure 2.—Relaxation curve at 291°K; ($[Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}]$) = 5.6 × 10^{-2} M; 0.5 M $HClO_4$: point a, initial absorbance; b, after first change; and c, final absorbance. Increasing absorbance is down on the vertical axis.

On the basis of the above observations, the mechanism is postulated to be

$$Fe(H_2O)_6^{3+} + Fe(CN)_6^{3-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Fe(H_2O)_6Fe(CN)_6 \qquad (2)$$

$$Fe(H_2O)_6Fe(CN)_6 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Fe(H_2O)_5Fe(CN)_6 + H_2O \qquad (3)$$

The species $Fe(H_2O)_6Fe(CN)_6$ is an ion pair and $K = [Fe(H_2O)_6Fe(CN)_6]/[Fe(H_2O)_6^{3+}][Fe(CN)_6^{3-}]$ is the equilibrium concentration quotient for reaction 2. The species represented by $Fe(H_2O)_5Fe(CN)_6$ is the actual complex in which cyanide bridges two iron(III) centers.

If reaction 3 equilibrates more slowly than reaction 2, then

$$\frac{1}{\tau_I} = k_{32} + \frac{k_{23}K([Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}])}{1 + K([Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}])}$$

A second relaxation time, $1/\tau_{II} = k_{21} + k_{12}([Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}])$, is associated with reaction 2 alone. However, this process appears to occur too rapidly to be observed by temperature-jump relaxation techniques (a to b in Figure 2). The observed relaxation process represented by $1/\tau_I$ should be linear in ($[Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}]$) when $K([Fe(H_2O)_6^{3+}] + [Fe(CN)_6^{3-}]) \ll 1$ and independent of ($[Fe(H_2O)_6^{3+}] +$

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[3] M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Part II, Chapter XVIII.

[4] R. Livingston, "Physico Chemical Experiments," 3rd ed, The Macmillan Co., New York, N. Y., 1948, p 44.

$[\text{Fe(CN)}_6^{3-}]$) when $K([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}]) \gg 1$. This behavior is observed in Figure 1.

Figure 3 presents plots of $\ln(k_{32}/T)$ and $\ln(k_{23}K/T)$ *vs.* $1/T$. The plots in Figure 1 yield k_{32} as the intercept and $k_{23}K$ as the slope of the initial linear portion. Values of k_{32} determined from Figure 1 are 15.0 ± 1.0 sec^{-1} (298°K), 9.5 ± 0.5 (291°K), and 6.2 ± 0.2 (282°K). The enthalpy and entropy of activation are 8.8 ± 0.6 kcal/mole and 5.5 ± 2.0 eu. Values of $k_{23}K$ are 1750 ± 250 M^{-1} sec^{-1} (298°K), 600 ± 80 (291°K), and 155 ± 25 (282°K), and the enthalpy of activation is 24.6 ± 1.6 kcal/mole. It should be recalled that the latter enthalpy value is the sum of the enthalpies corresponding to k_{23} and K. The errors in $k_{23}K$ are large because of the error in points at such low values of $([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}])$. Values of k_{23} can in principle be determined at large values of $([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}])$ where $1/\tau_{\text{I}}$ approaches $k_{23} + k_{32}$. However, in this region the effect is very small and it can only be said that $1/\tau_{\text{I}}$ does not increase appreciably above the value at $([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}]) = 17.0 \times 10^{-2}$ M. Therefore it has been necessary to estimate values of k_{23} and thus K at various temperatures from the curve which gives a best fit of the experimental data. Values of k_{23} and K obtained at various temperatures from the best fit of the data in Figure 1 (solid lines) are: 50 sec^{-1} and 35 M^{-1} (298°K), 36 sec^{-1} and 17 M^{-1} (291°K), and 25 sec^{-1} and 6.5 M^{-1} (282°K). It should be noted that in the region where $([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}])$ is large (greater than 5×10^{-2} M in Figure 1) $1/\tau_{\text{I}}$ is most sensitive to changes in k_{23} and K. Since this is the region where errors in $1/\tau_{\text{I}}$ are largest, values of k_{23} and K are probably not good to more than 20%. Figure 3 includes a plot of $\ln(k_{23}/T)$ *vs.* $1/T$. The enthalpy of activation determined from this plot is estimated to be 7 ± 2 kcal/mole. Recall that the error is calculated from one-fourth of the limits of uncertainty of the plot. The entropy of activation is −26 ± 7 eu.

Discussion

The detailed mechanism by which a ligand (in this case Fe(CN)_6^{3-}) enters the first coordination sphere of hexaaquoiron(III) has been a subject of continuing interest.[5-7] It appears in the case of the hexaaquoiron(III)–hexacyanoferrate(III) reaction that the mechanism involves ion-pair formation followed by replacement of water by the ligand as the rate-determining step. This behavior generally occurs in complex formation between +2 transition metal ions and ligands.[8] In the case of +2 transition metal ions the rate constant corresponding to k_{23} is comparable to the rate constant for solvent exchange of the aquated metal ion. The rate constant for water exchange of hexaaquoiron(III) has been measured by Connick and his co-workers to be 1.6×10^4 sec^{-1} at 298°K where any coordinated water can be replaced.[9] The value of 50 sec^{-1} reported in this study is considerably smaller than the water-exchange rate constant. If the rate constants for complex formation in the $\text{Fe(H}_2\text{O)}_6^{3+}$–$\text{SCN}^-$, –$\text{Br}^-$, and –$\text{Cl}^-$ systems—127,[10] 20,[11] and 9.4 M^{-1} sec^{-1} [12] at 298°K—are assumed to be composed of an ion-pairing constant and a rate constant corresponding to k_{23} in this system, it is possible to calculate the rate constants corresponding to k_{23} for these systems if the ion-pairing constants are known. Values of the corresponding ion-pairing constants have been determined for the $\text{Cr(H}_2\text{O)}_6^{3+}$–$\text{SCN}^-$ and –Cl^- systems.[13] These should not be appreciably different from the values for the $\text{Fe(H}_2\text{O)}_6^{3+}$ systems. Values at 298°K and 1 M NaClO_4 are approximately 1 M^{-1} for $\text{Cr(H}_2\text{O)}_6^{3+}$–$\text{SCN}^-$ and 1.5 M^{-1} for $\text{Cr(H}_2\text{O)}_6^{3+}$–$\text{Cl}^-$. Certainly the ion-pairing constant for $\text{Cr(H}_2\text{O)}_6^{3+}$–$\text{Br}^-$ should be of the same magnitude. Thus the rate constants in these systems, which are analogous to k_{23} in the $\text{Fe(H}_2\text{O)}_6^{3+}$–$\text{Fe(CN)}_6^{3+}$ system, fall well below the water-exchange rate constant for hexaaquoiron(III) and are in the range 10–127 sec^{-1}.

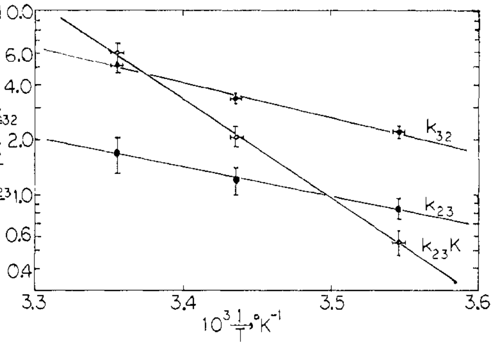

Figure 3.—Plots of $\ln(k_{22}/T)$, $\ln(k_{23}K/T)$, and $\ln(k_{23}/T)$ *vs.* $1/T$.

It might be reasonable to use the terms "loose" and "tight" ion pairs to express the distinction seen between the +2 transition metal ion systems where the values of the rate constant corresponding to k_{23} approach the water-exchange value and the iron(III) systems. In the iron(III) system the water in the ion pair may in a sense be "trapped" between the iron(III) of hexaaquoiron(III) and hexacyanoferrate(III).

The value of K obtained, 35 M^{-1} at 298°K, seems reasonable when compared with ion-pairing concentration quotients between +3 ligands with an inert first-coordination sphere (*e.g.*, $\text{Cr(H}_2\text{O)}_6^{3+}$ and $\text{Co(NH}_3)_4^{3+}$) and negatively charged ligands.[13]

It is possible to set limits on the values of k_{12} and k_{21} (reaction 2). Since $1/\tau_{\text{II}} = k_{21} + k_{12}([\text{Fe(H}_2\text{O)}_6^{3+}] + [\text{Fe(CN)}_6^{3-}]) > 10^6$ sec^{-1} and $K = k_{12}/k_{21}$ is 35 M^{-1}, $k_{21} > 10^6$ sec^{-1} and thus $k_{12} > 3.5 \times 10^7$ M^{-1} sec^{-1}.

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Complexes of Sulfoxides. I. Octahedral Complexes of Manganese(II), Iron(II), Cobalt(II), Nickel(II), and Zinc(II)

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Eighteen octahedral manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) complexes of RR'SO (where R and R' are phenyl, phenyl and methyl, *n*-propyl, and *n*-butyl) have been synthesized. The manganese(II), cobalt(II), and nickel(II) complexes exhibit normal high-spin magnetic behavior. From infrared spectra it is inferred that all of the ligands coordinate through the oxygen. The S–O stretching vibration frequency of 1055 to 1011 cm^{-1} in the ligand is reduced to 990–968 cm^{-1} in the complexes. The downward shift relative to the free ligand is 28–58 cm^{-1}. Selected infrared bands in the ligands and complexes are assigned.

Introduction

Since 1960 a considerable amount of literature[2-13] has been published on dimethyl sulfoxide and tetramethylene sulfoxide complexes of the first transition series, platinum(II), and palladium(II). A recent preliminary report[14] includes the synthesis of octahedral complexes of diphenyl sulfoxide with members of the first transition series. Early general agreement based on infrared studies that oxygen acts as a donor atom toward members of the first transition series and that sulfur is the donor atom in platinum(II) and palladium(II) complexes has been verified. Bennett, Cotton, and Weaver[12] found that the conclusions from infrared studies are correct for *trans*-$[FeCl_2((CH_3)_2SO)_4][FeCl_4]$ and *trans*-$[PdCl_2((CH_3)_2SO)_2]$.

There is some disagreement regarding the assignment of the S–O stretching and CH_3 rocking vibrations in dimethyl sulfoxide oxygen-bonded complexes. Some authors[5,6] assign the S–O stretching fundamental to a band near 1000 cm^{-1} and the CH_3 rocking vibration to a band near 930 cm^{-1}. Other authors[4,8,11] reverse the assignments. Because the S–O stretching fundamental and the methyl group vibrations are coupled in dimethyl sulfoxide,[15] the assignments are uncertain.

It has been suggested[3] that the frequency shift of the S–O stretching vibration upon oxygen coordination is proportional to the strength of the metal–oxygen bond. Based on this assumption, the following stability order[6] has been proposed for dimethyl sulfoxide complexes with perchlorate anions: copper(II) > lead(II) > iron(II) > cobalt(II) > manganese(II) > nickel(II).

Experimental Section

The synthetic methods of 18 complexes representing five different metals with various sulfoxide ligands are listed in Table I along with their colors, melting points, and elemental analyses.

Chemicals.—The following chemicals were obtained from the Aldrich Chemical Co., Inc.: di-*n*-propyl sulfoxide, di-*n*-butyl sulfoxide, and diphenyl sulfoxide. Dimethyl sulfoxide was obtained from the Crown Zellerbach Chemical Products Division and phenyl methyl sulfoxide was a gift from Dr. K. K. Andersen.[16] The hydrated metal perchlorate salts were obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. All other chemicals were of reagent grade quality. Liquid sulfoxides were dried over barium oxide and in some cases were vacuum distilled.

Synthetic Method A.—This was based on the procedure given by Meek, Drago, and Piper.[10] The appropriate hydrated perchlorate salt (0.002 mole) was dissolved in a minimum amount of methanol. A 0.02 molar quantity of 2,2-dimethoxypropane was added to this solution and to a second flask containing the appropriate ligand (0.012 mole). Both flasks were stoppered and stirred at 40° for 2.5 hr. The ligand solution was added to the metal ion solution and the resulting mixture was stirred for an additional 30–60 min. In the instances where crystalli-

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[1] (a) This report is based on a thesis submitted by William F. Currier to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements of the Master of Science degree; (b) author to whom correspondence should be addressed.

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