^{18}O-Isotope-Induced Shifts in ^{15}N Nuclear Magnetic Resonance Spectroscopy. 1. Isotope Shift in Nitrite and Its Application to the Study of Oxygen Exchange of Sodium [^{15}N,$^{18}O_2$]Nitrite

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Abstract: Substitution of ^{18}O for ^{16}O results in an upfield shift in the ^{15}N nuclear magnetic resonance signal of the ^{15}N-enriched nitrite and nitrate ions. The magnitude of the shift in the ^{15}N NMR signal depends on the number of ^{18}O atoms covalently bonded to the nitrogen atom. In nitrite the shift is 0.138 ppm/^{18}O. This relatively large isotope shift permits the direct study by nuclear magnetic resonance spectroscopy of oxygen-exchange reactions involving nitrogen species. Acid-catalyzed medium nitrite(oxygen)-water exchange was followed in a continuous assay mode to demonstrate the ease and applicability of the isotope shift to the study of nitrogen(oxygen)-water exchange reactions. It was found that at pH 6.26 and 28 °C a sequential mode of exchange of the oxygen atoms is observed. This observation agreed with a mechanism postulated earlier on the basis of indirect evidence.

Oxygen-18 has been shown to exert detectable isotope effects on the NMR signals of many different nuclei covalently bonded to the oxygen-18 atom. Substitution of an oxygen-18 atom for an oxygen-16 typically results in an upfield shift in the NMR signal. The magnitude of this isotope shift depends on many factors including the chemical shift range of the nucleus, the structure of the molecule, and solvent effects. In ^{1}H NMR, for example, dilute solutions of $H_2{}^{18}O$ in dioxane-$CDCl_3$ displayed a significantly greater isotope shift than neat samples of $H_2{}^{18}O$ relative to $H_2{}^{16}O$.[1,2] The ^{18}O-labeled permanganate ion shifted the ^{55}Mn NMR signal upfield 0.59 ppm/^{18}O.[3,4] Likewise, the ^{95}Mo NMR signal in the molybdate ion was shifted upfield 0.25 ppm/^{18}O upon substitution of ^{18}O for ^{16}O.[4] Recently the ^{18}O-isotope effect in ^{31}P NMR was reported to be 0.020 ppm/^{18}O in inorganic phosphate.[5,6] The isotope-induced shift in ^{31}P NMR has found extensive use as a technique for studying problems of biochemical interest. The latest isotope effects on NMR signals which have been reported were an ^{15}N shift in ^{13}C NMR, chlorine and bromine isotope shifts in ^{195}Pt NMR, and an anomalous deuterium effect in ^{1}H NMR.[7] The broadly applicable ^{18}O shift in ^{13}C NMR has recently been described by us.[8] This isotope effect is now being characterized as to its physical properties and has already found use as an experimental technique for establishing stereochemical relationships and studying a variety of oxygen-exchange and biosynthetic problems.[9]

In light of the recent observations that ^{18}O exerts an observable isotope effect in ^{31}P and ^{13}C NMR spectroscopy we felt it likely that ^{18}O should exert an observable isotope effect on a number of other commonly encountered nuclei which display NMR signals. The possible existence of an ^{18}O-isotope effect in ^{15}N nuclear magnetic resonance spectroscopy appeared to be of particular interest and utility. Consequently, we prepared ^{18}O-labeled silver nitrite starting with the ^{15}N-enriched sodium nitrite salt and subjected this compound to ^{15}N NMR analysis. This paper reports the results of this investigation, which clearly demonstrates that ^{18}O does exert an observable isotope effect on ^{15}N NMR signals.

The existence of this isotope effect provides a means whereby for the first time the direct observation and quantitation of acid-catalyzed medium nitrogen(oxygen)-water exchange reactions can be easily achieved. As a result the pathway or mode of oxygen exchange can be demonstrated, which heretofore has been hypothesized from indirect data, but which had never been observed directly. We also report in this paper the results of our investigation of acid-catalyzed medium nitrite(oxygen)-water exchange, which we have followed for the first time directly by ^{15}N NMR. Previously this reaction had been analyzed by mass spectrometry, which generally involved chemical conversion of a nonvolatile reactant or reaction product to a suitable volative derivative such as N_2O or CO_2. Although this method does reveal whether or not medium nitrite(oxygen)-water exchange has taken place, it suffers from two inherent limitations: (1) the mode of oxygen exchange cannot be ascertained directly and therefore must be deduced from the indirect evidence and (2) often the procedures necessary to obtain volatile derivatives are time consuming and may be accompanied by experimental artifacts which affect the results if proper controls are not utilized. The direct analysis of medium nitrogen(oxygen)-water exchange reactions by ^{15}N NMR as illustrated in the present study will avoid most such limitations.

Experimental Section

Synthesis of Silver [^{15}N,$^{18}O_2$]Nitrite. Silver [^{15}N,$^{18}O_2$]nitrite was synthesized[10,11] by dissolving sodium [^{15}N]nitrite (95 atom % ^{15}N, Merck) (1.0 g, 0.014 mol) in 2.0 mL of [^{18}O]water (99 atom % excess ^{18}O, normalized, Norsk Hydro, Oslo) and acidifying with 0.1 mL of 70% perchloric acid. The solution was capped and stored overnight at room temperature. To this solution was added 1.0 mL of an equimolar solution of silver nitrate. Silver [^{15}N,$^{18}O_2$]nitrite precipitated immediately. The pale yellow crystals were collected on a funnel, washed with ethanol and ether, air-dried, and stored in an amber bottle. Analysis of the salt by ^{15}N NMR showed 77% ^{18}O enrichment, specifically 61% $^{18}O_2$, 33% $^{18}O^{16}O$, and 6% $^{16}O_2$. (The ^{18}O enrichment expected on the basis of complete equilibration was 76%.)

Synthesis of Sodium [^{15}N,$^{18}O_2$]Nitrite. Sodium [^{15}N]nitrite (95 atom % ^{15}N, Merck) (0.95 g, 0.013 mol) was dissolved in 2.0 mL of [^{18}O]-water, and the solution was acidified with 0.1 mL of 70% perchloric

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(1) Pinchas, S.; Mesulan, E. *J. Chem. Soc., D* **1970**, 1147-1148.

(2) Sredni, B.; Pinchas, S. *J. Magn. Reson.* **1972**, *7*, 289-290.

(3) Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Z. Naturforsch., A* **1976**, *31A*, 1427-1428.

(4) Buckler, K. U.; Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Z. Naturforsch., A* **1977**, *32A*, 126-130.

(5) Cohn, M.; Hu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 200-203.

(6) Lutz, O.; Nolle, A.; Staschewski, D. *Z. Naturforsch., A* **1978**, *33A*, 380-382.

(7) Wasylishen, R. E.; Muldrew, D. H.; Friesen, K. J. *J. Magn. Reson.* **1980**, *41*, 341-342. Ismail, I. M.; Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1175-1176. Yonemitsu, T.; Kubo, K. *Ibid.* **1981**, 309.

(8) Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 252-253.

(9) Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4389-92, and references cited therein.

(10) Anbar, M.; Halmann, M.; Pinchas, S. *J. Chem. Soc.* **1960**, 1242-1245.

(11) Bunton, C. A.; Llewellyn, D. R.; Stedman, G. *J. Chem. Soc.* **1959**, 568-573.

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acid.[10,11] The capped, acidified mixture was allowed to incubate overnight. The acid was neutralized by adding an equimolar amount of solid sodium hydroxide, and the solution was stored in the dark. Sodium [^{15}N,$^{18}O_2$]nitrite is stable in this nonacidic solution, and no significant oxygen exchange takes place over several weeks. By ^{15}N NMR the ^{18}O enrichment was 63%, specifically 40% $^{18}O_2$, 45% $^{18}O^{16}O$, and 15% $^{16}O_2$.

Instrumentation. The ^{18}O-isotope-induced shift on the ^{15}N NMR signal and the exchange reaction were measured and followed on an NTC-470 spectrometer fitted with an 8-mm probe, operating at 47.6 MHz. A 90° pulse angle, 1000- or 2000-Hz sweep width, 16K data block, and 0.5-Hz line-broadening factor were used in the single-pulse experiment. The probe temperature was 28 °C. The isotope-induced shift was also confirmed on a Varian FT-80A spectrometer.

Kinetics of Medium Nitrite(Oxygen)-Water Exchange. Distilled, deionized water was used to prepare the exchange solution. A Corning Model 130 pH meter was used to measure the solution pH. A 1.3×10^{-3}-mol sample of sodium [^{15}N,$^{18}O_2$]nitrite was added to a mixture of 25% deuterium oxide (99.75 atom % ^2H, Baker) in a total volume of 4.0 mL in an 8-mm NMR tube. The pH was adjusted to 6.26 with 70% perchloric acid and 2 M NaOH. Following temperature equilibration, spectra were taken at regular intervals.

Data Analysis for Medium Nitrite(Oxygen)-Water Exchange. Acid-catalyzed medium nitrite(oxygen)-water exchange is analogous to acid-catalyzed medium carboxyl(oxygen)-water exchange described previously.[9] The reaction can be described as in eq 1. In a large molar excess

$$HN^{18}O_2 \xrightarrow{H_2O} HN^{18}O^{16}O \xrightarrow{H_2O} HN^{16}O_2 \qquad (1)$$

of unlabeled (^{16}O) water the reaction is assumed to be effectively irreversible. For a given rate constant, k, the probability that an ^{18}O atom will be lost by an exchange reaction can be expressed as in eq 2. The

$$HN^{18}O_2 \xrightarrow{k} HN^{18}O^{16}O \xrightarrow{{}^1\!/_2 k} HN^{16}O_2 \qquad (2)$$

set of linear differential equations which describes the reaction in eq 2 is shown in eq 3, where N^2 represents [$HN^{18}O_2$], N^1 represents

$$\begin{aligned} dN^2/dt &= -kN^2 \\ dN^1/dt &= -{}^1\!/_2 kN^1 + kN^2 \qquad (3) \\ dN^0/dt &= {}^1\!/_2 kN^1 \end{aligned}$$

[$HN^{18}O^{16}O$], and N^0 represents [$HN^{16}O_2$], and the concentrations are expressed as fractional proportions. The differential equations in (3) are solved by the variation of parameters method to yield

$$N^2(t) = N^2(0)e^{-kt} \qquad (4a)$$

$$N^1(t) = [N^1(0) + 2N^2(0)]e^{-0.50kt} - 2N^2(0)e^{-kt} \qquad (4b)$$

$$N^0(t) = [N^0(0) + N^1(0) + N^2(0)] - [N^1(0) + 2N^2(0)]e^{-0.50kt} + N^2(0)e^{-kt} \qquad (4c)$$

where $N^n(0)$ for n = 0, 1, and 2 is the initial concentration of that isotopic species.

By definition, the total percentage oxygen-18 content, N_T, present at any time t is

$$N_T = 100\sum_{n=0}^{2} nN^n(t) = 100[N^1(0) + 2N^2(0)]e^{-0.50kt} \qquad (5)$$

A plot of the natural logarithm of N_T against t will give a slope equal to $-0.50k$, and the pseudo-first-order rate constant, k, may be calculated. The theoretical curves based on this value of k may be calculated for each of the isotopic species present by using eq 4 in order to compare them to the experimental data.

Results

Figure 1 illustrates the upfield ^{18}O-isotope shift exhibited by the silver [^{15}N,$^{18}O_2$]nitrite salt. The shift is 0.138 ± 0.001 ppm/^{18}O. The same shift is observed for the sodium [^{15}N,$^{18}O_2$]nitrite salt. The unlabeled (^{16}O) species has arbitrarily been assigned the value of 0.000 ppm, and upfield shifts are positive.

The series of spectra obtained for the exchange reaction was deconvoluted on a Nicolet 1180 computer. The area under each peak was calculated as a fractional part of the whole spectrum with an error of ±2%. Nitrite(oxygen)-water exchange catalyzed by acid at pH 6.26 (in 25% deuterium oxide) and at 28 °C can be described by eq 4a-c and proceeds with a pseudo-first-order rate constant of 7.8 (±0.4) × 10^{-6} s^{-1}. Figure 2 exemplifies the relationship between the experimental data and the theoretical curves calculated for the medium nitrite(oxygen)-water-exchange reaction by using the procedure described in the Experimental Section. The concentrations of the isotopic species are expressed in terms of percentages which are in turn obtained by multiplying the proportions calculated from eq 4 by 100.

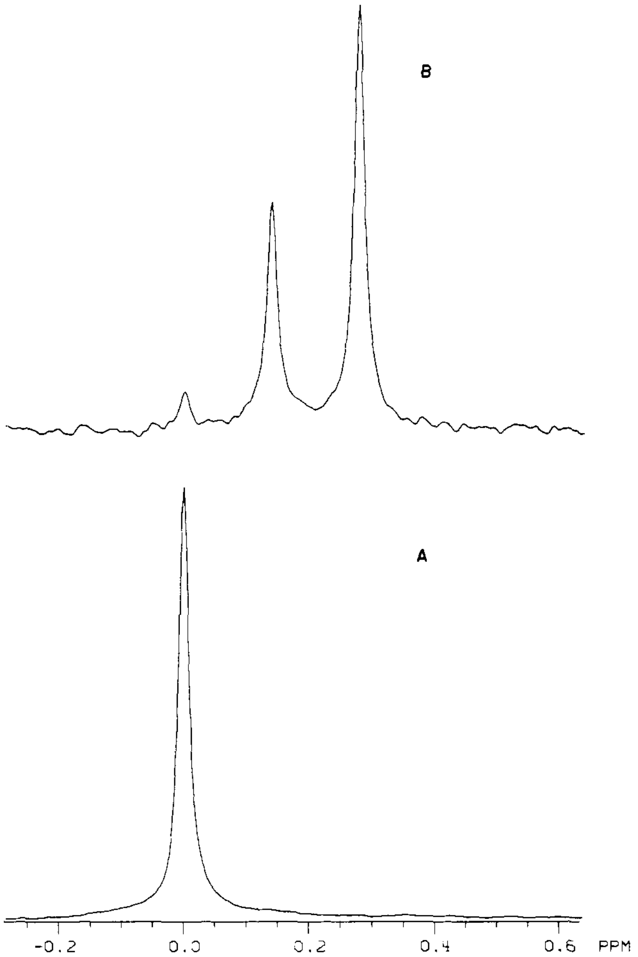

Figure 1. An upfield shift in the ^{15}N NMR signal of the nitrite ion of 0.138 ppm (per ^{18}O) occurs upon substitution of ^{18}O for ^{16}O. (A) Sodium [^{15}N]nitrite (95 atom % ^{15}N) starting material: 1.0 g dissolved in 4.0 mL of ^2H_2O. (B) Silver [^{15}N,$^{18}O_2$]nitrite (95 atom % ^{15}N, 77 atom % ^{18}O): 0.5 g of silver [^{15}N,$^{18}O_2$]nitrite in 3.0 mL of NH_4OH and 1.0 mL of ^2H_2O. The percentages of the ^{18}O-labeled nitrite species are 6% $^{15}N^{16}O_2$, 33% $^{15}N^{16}O^{18}O$, and 61% $^{15}N^{18}O_2$.

Discussion

Figure 1 clearly demonstrates that ^{18}O does exert an isotope effect on the ^{15}N NMR signal of the nitrite ion.[12] Replacement of chemically equivalent ^{16}O atoms by ^{18}O atoms results in an upfield shift in the ^{15}N NMR signal of the covalently bonded nitrogen atom. The magnitude of this NMR shift depends on the number of ^{18}O atoms and for the nitrite ion the observed shift is 0.138 ppm/^{18}O. To date, no theoretical estimates have been made of the ^{18}O-isotope effect in ^{15}N NMR; however the lone pair of electrons on the nitrite ion may possibly play a significant role in the isotope effect due to a very large paramagnetic contribution to the shielding.

The reaction mechanisms of a number of inorganic nitrogen compounds have recently been reviewed by Stedman[13] and in-

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[12] In experiments in progress, we have determined that the ^{18}O shift in ^{15}N nitrate is 0.056 ppm/^{18}O. Thus, the magnitude of the ^{18}O shift depends on the chemical nature of the nitrogen species. We are presently applying this observation in the study of acid-catalyzed medium nitrate(oxygen)-water exchange. The results of these investigations will be published at a later date.

[13] Stedman, G. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 113-170.

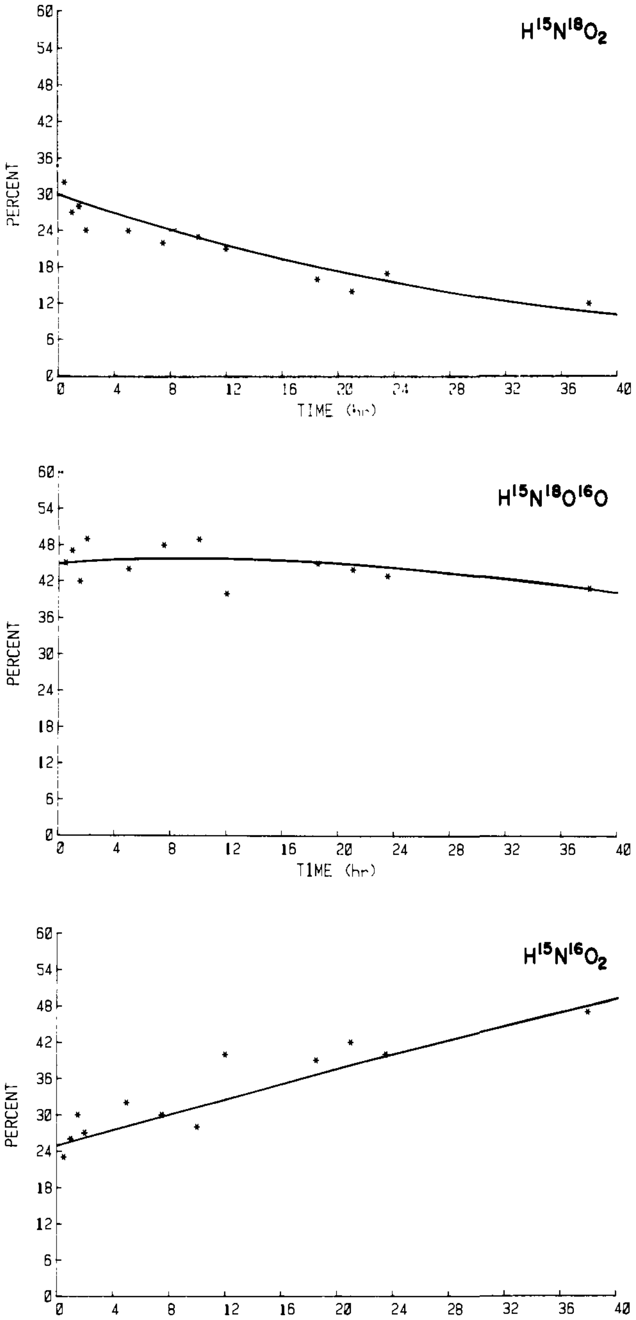

Figure 2. The experimental data and the corresponding calculated theoretical curves are plotted for acid-catalyzed nitrite(oxygen)–water exchange for the three ^{18}O-labeled nitrite species. The data are from the ^{15}N NMR spectra of a solution of 1.3 × 10^{-3} mol of sodium [^{15}N,$^{18}O_2$]nitrite in 4.0 mL of solvent (25% deuterium oxide), pH 6.26, incubated at 28 °C. The theoretical curves are calculated on the basis of a sequential mechanism of exchange with a rate constant of 7.8 × 10^{-6} s^{-1}.

cluded in the review were references to those papers dealing with nitrogen(oxygen)–water exchange appropriate to the topic. One medium nitrogen(oxygen)–water exchange reaction which has been studied in some detail is medium nitrite(oxygen)–water exchange. The existence of an easily measurable ^{18}O-isotope effect in ^{15}N NMR readily provides a means for the direct quantitation of this acid-catalyzed oxygen-exchange reaction at nitrogen, which is illustrated below.

Acid-catalyzed medium nitrite(oxygen)–water exchange reactions have been followed by the mass spectrometric analysis of the ^{18}O content of N_2O or CO_2. Anbar and Taube[14] prepared the volatile N_2O for analysis by reacting nitrous acid with hydrogen azide ($HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O$). This azide method was also used by Bunton and Stedman[15] to measure the rate of the exchange reaction; however they discovered that this method of analysis has a very serious limitation. They found that solvent water can exchange with the nitrous acid during the synthesis of the N_2O from HNO_2 and HN_3; thus a correction must be made to the mass spectral data to account for this exchange. Bunton et al.[11] also measured the rate of the exchange reaction by isolating the silver nitrite salt. The salt was decomposed by heating with NH_4Cl to give water which was equilibrated with CO_2. The CO_2 was subjected to mass spectrometric analysis. These methods at best only provide data on the average ^{18}O content and do not afford information about the concentrations of individual nitrite species. Such information is available by using the direct method of ^{15}N NMR illustrated here.

Under some conditions of pH, the nitrite ^{15}N NMR signal exhibits exchange broadening. At pH <6 the signal is broadened such that no individual isotopically labeled nitrite species can be resolved. In solutions of pH >6 the isotopically labeled nitrite species can be resolved, although some exchange broadening of the signals is still evident between pH 6 and 7. In basic solution no exchange broadening is observed. Unfortunately the exchange broadening severely limits the power of ^{15}N NMR to follow acid-catalyzed medium nitrite(oxygen)–water exchange reaction in a continuous assay mode. Medium nitrite(oxygen)–water exchange reactions may nevertheless be studied even in very acidic media, although the NMR assays must necessarily be discontinuous. Briefly, the discontinuous assay method involves incubating the substrate under specified conditions, removing aliquots of the exchange solution at given time intervals, and adjusting the pH to neutral or basic conditions for ^{15}N NMR analysis. The nitrogen substrate is stable under these basic conditions and does not undergo subsequent exchange reactions to a significant degree. Despite this requirement for discontinuous assays under some conditions of pH, analysis by ^{15}N NMR is more convenient than mass spectrometry, eliminates the uncertainty of extraneous reactions during conversion to volatile derivatives, and offers the important advantage of measuring the relative ratios of the different isotopic species rather than an average ^{18}O content.

Medium nitrite(oxygen)–water exchange has been found to be very sensitive to pH, the rate decreasing with increasing pH. Furthermore, the rate of the exchange is dependent on the concentration of the nitrous acid, on the ionic strength of the solution, and on the nucleophilicity of added anions. This evidence as well as other evidence[13] has been used to postulate that the reaction mechanism in dilute nitrite solutions involves a rapid protonation of nitrous acid to give the nitrous-acidium ion ($H_2NO_2^+$) and a rate-determining dehydration to the nitrosonium ion (NO^+)

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \qquad (6)$$

The formation of the nitrosonium ion has been disputed (see ref 13 for a summary of the arguments); thus presumably exchange would occur by nucleophilic attack of a water molecule on the nitrous-acidium ion. We have observed in a continuous assay mode that at pH 6.26 in 25% deuterium oxide and at 28 °C acid-catalyzed medium nitrite(oxygen)–water exchange proceeds by the sequential exchange mode illustrated by eq 1. The data for the exchange reaction and the theoretical curves calculated for the sequential exchange mode are graphically shown in Figure 2. The agreement beween the theoretical curves and the experimental data support the sequential exchange mode as well as the assumption of effective irreversibility. This observation supports the hypothesized reaction mechanism of formation of the nitrous-acidium ion; however, it does not distinguish between the dehydration of the ion to nitrosonium ion and rehydration to nitrous-acidium ion and direct nucleophilic attack by water on the nitrous-acidium ion. Both mechanisms are plausible as shown by eq 7a,b.

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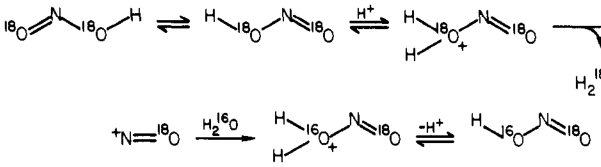
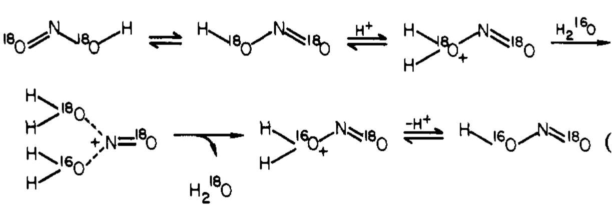
(14) Anbar, M.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 6243–6247.

(15) Bunton, C. A.; Stedman, G. *J. Chem. Soc.* **1959**, 3466–3474.


(7a)


(7b)

We have demonstrated that ^{18}O does exert an isotope effect on the ^{15}N NMR signal of the ^{15}N-enriched, ^{18}O-labeled nitrite ion. The magnitude of the isotope-induced shift was 0.138 ppm/^{18}O, and the isotope shift was additive. We have also shown that the ^{18}O-isotope effect in ^{15}N NMR can be applied to the field of physical–inorganic chemistry. Nitrogen(oxygen)–water exchange reactions can be followed in greater detail than has been possible previously since ^{15}N NMR permits a direct quantitation of the different ^{18}O-isotopically labeled nitrogen species. This new technique was used to examine an acid-catalyzed medium nitrite(oxygen)–water exchange reaction in a continuous assay mode. The exchange was found to proceed by the sequential exchange mode as had been previously postulated from indirect evidence on the basis of the total ^{18}O content of the nitrite ion. We believe that the ability to directly quantitate the different isotopically labeled nitrogen species will provide an opportunity to study nitrogen(oxygen)–water exchange reactions in detail which heretofore has not been possible. In addition to mechanistic organic and physical–inorganic studies, applications may also be anticipated in many biological areas.

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Use of Magnetic Circular Dichroism to Determine Axial Ligation for Some Sterically Encumbered Iron(II) Porphyrin Complexes

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Abstract: The application of magnetic circular dichroism (MCD) as a fingerprint method for determining the spin state and axial coordination environment of a number of synthetic ferrous porphyrin complexes has been examined. The appearance of the MCD spectrum is a function of the spin state and the nature of the axial ligand or ligands. When these variables remain constant, the band shapes in the Soret region, but not the intensities, do not differ significantly within the series of porphyrins investigated here. For any given axial ligand or ligands, provided that spectra have been measured for a known example of each possible spin state and coordination environment to serve as standards, the shape of the MCD Soret band can be used as a qualitative marker of these key parameters. This determination is made on the basis of a single spectrum, and the advantages over other methods derive from the unique simplicity of the measurement. The coordination chemistry at iron(II) in the family of capped, pocket, and cofacial porphyrins studied here, as followed by MCD, can be used to determine, in a semiquantitative manner, the effects of the steric control of coordination features specifically incorporated into these porphyrin molecules. The design features and the steric effects are discussed. The MCD spectra are presented in graphic and tabular form, and the advantages and limitations of MCD as employed here are considered. The preparation and characterization of a mixed-metal, free-base, cofacial porphyrin is presented.

Introduction

Nature has chosen iron porphyrins to function at the active site in a number of biological systems that are indispensable to most forms of animal life.[2] These complex systems continue to inspire porphyrin-related research. Some quantity of the mechanics and properties of these systems can be ascribed to the various discernible features of metallochemistry, such as oxidation state, redox processes, type of ligation, ligand affinity, coordination number, and spin state. These properties are often influenced or controlled by interactions between the heme and the protein component. In order to learn more about heme–protein interactions associated with the activation, transfer, and storage of dioxygen, we, and others, have constructed synthetic analogues of the oxygen-binding centers in hemoproteins. These previously reported studies[3] have provided some assistance to our understanding of hemoproteins and have suggested new avenues of research.

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(1) (a) Stanford University. (b) Northwestern University. (c) University of South Carolina. (d) University of Minnesota.

(2) (a) Dolphin, D., Ed. "The Porphyrins"; Academic Press: New York, 1979; Vols. VI, VII. (b) Smith, K. M., Ed. "Porphyrins and Metalloporphyrins"; Elsevier: Amsterdam, 1975.

(3) (a) Collman, J. P.; Halbert, T. R.; Suslick, K. S. In "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley: New York, 1980. (b) Ellis, P. E., Jr.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889, and references therein. (c) Linard, J. E.; Ellis, P. E., Jr.; Budge, J. E.; Jones, R. D.; Basolo, F. *Ibid.* **1980**, *102*, 1896, and references therein. (d) Traylor, T. G.; Berzinis, A. P. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3171, and references therein.

0002-7863/81/1503-5636$01.25/0