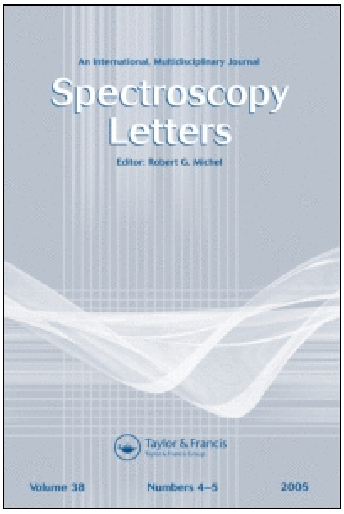

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Rapid Simultaneous Measurement of Hydrogen Isotopes in Aqueous Solution by ^{31}P NMR

Josann A. Valley[a]; Ronald F. Evilia[a]
[a] Department of Chemistry, University of New Orleans New Orleans, La.

To cite this Article Valley, Josann A. and Evilia, Ronald F.(1989) 'Rapid Simultaneous Measurement of Hydrogen Isotopes in Aqueous Solution by ^{31}P NMR', Spectroscopy Letters, 22: 5, 541 — 547

To link to this Article: DOI: 10.1080/00387018908053903

URL: http://dx.doi.org/10.1080/00387018908053903

SPECTROSCOPY LETTERS, 22(5), 541-547 (1989)

RAPID SIMULTANEOUS MEASUREMENT OF HYDROGEN ISOTOPES IN AQUEOUS SOLUTION BY ^{31}P NMR

Key Words: NMR, Deuterium, Aqueous, Rapid, ^{31}P, Phosphorous Acid

Josann A. Valley and Ronald F. Evilia

Department of Chemistry
University of New Orleans
New Orleans, La. 70148

Abstract: Integration of the ^{31}P spectrum of phosphite formed after reaction of phosphorus tricholoride with partially deuterated water is found to yield an accurate measurement of the percent of deuteration (or protonation) after correction for the kinetic isotope effect. A kinetic isotope effect favoring proton reaction by a factor of 3.2 ± .25 is found. The method is tested over the range of 10% to 90% deuterium. The results are found to be accurate to ± 6% relative, which is probably limited by experimental error in the determination of the integral. Measurements outside the 10 to 90% range are possible, but require longer acquisition times because of the low signal-to-noise ratio of the small peaks.

INTRODUCTION:

In principle the determination of ^{1}H and ^{2}H is possible by nuclear magnetic resonance spectroscopy if one adds some standard compound to the sample to provide an intensity standard or by a method of standard additions.

Because proton NMR is more common and easily performed than deuterium NMR, the direct NMR determination of ^1H in deuterated samples has been reported.[1-3] The direct method is most suitable for small amounts of ^1H in highly deuterated solvents because of the difficulty of accurately measuring absolute values of very large numbers or because of difficulty in doing a standard addition extrapolation from high concentrations. Leyden and Reilley reported a method for determining both ^1H and ^2H from the proton spectrum of non-labile hydrogens of benzyl-amines.[4] In this method, the splitting of the benzyl CH_2 into a doublet by ^1H and a poorly resolved 1:1:1 triplet by ^2H upon protonation (or deuteration) of the amine in highly acidic solution provides integrable signals whose intensities are proportional to the percentage of ^1H and ^2H respectively. Although this method is superior to the direct method because it provides a measurement of both isotopes and does not require any intensity standard, four serious problems limit its utility. First, the separation of the protium doublet from the deuterium triplet is small making it difficult to accurately measure the integrals; second, the coupling is only observed when proton (or deuteron) exchange with the amine is slow (i.e. in highly acidic solutions); third, the presence of a large water peak in mixtures containing significant amounts of ^1H is a serious source of error; and finally, the presence of other compounds having signals in the region of the CH_2 resonance cannot be tolerated.

In this communication we report an improvement in the method of Leyden and Reilley that overcomes all of the disadvantages mentioned above. In this method PCl_3 is reacted with the aqueous solution to produce phosphorous and hydrochloric acids. Since one of the hydrogens of phosphorous acid is bonded to the phosphorus and is inert to chemical exchange on a time scale much longer than the NMR time scale, the ^{31}P NMR spectrum shows coupling to either ^1H or ^2H depending upon whether it was formed by reaction with ^1H_2O or ^2H_2O. The large ^1J coupling constants characteristic of ^{31}P NMR spectra result in widely spaced peaks that are easily integrated for quantitative analysis.

EXPERIMENTAL:

Aqueous mixtures varying from 10% deuterium to 90% deuterium were prepared by weight from 99.8% deuterium oxide (Norell, Inc.) and distilled water. The phosphorus trichloride was obtained as a 2 M solution in methylene chloride from Aldrich Chemical Co. Samples were prepared by reacting 0.5 mL of the PCl_3 solution, removed from the sealed vial with a nitrogen filled syringe, with 1.0 mL of the aqueous solution at room temperature. The ^{31}P NMR spectrum of the aqueous layer of each sample was obtained immediately after reaction or, if it was not possible to obtain the spectrum immediately, the sample was stored at $0^{o}C$ until the spectrum could be acquired.

All spectra were acquired with a JEOL, Inc. FX90Q FTNMR spectrometer. A transmitter pulse of approximately 60^{o} (20 microseconds) and a pulse delay of 10 seconds were employed for the data acquisition. Spectral acquisition consisted of 4K real points and 4K zero filling. Fifty spectra were averaged for each data point. All spectral widths were 1500 Hz (41.4 ppm) and a 1.7 Hz apodization was applied to all of the data sets prior to Fourier transformation. Spectra were integrated by the FX90Q software. The ratio of the deuterium triplet integral to the proton doublet was recorded.

RESULTS AND DISCUSSION

Figure 1 shows representative spectra for several levels of deuteration. The widely spaced doublet (J = 690 Hz) arising from the protonated phosphorous acid is clearly separated from the 1:1:1 triplet (J = 106 Hz) of the deuterated compound. Visual examination of the spectra and quantitative comparison of the relative integrated intensities in every case indicated that the deuterium signal was significantly less than predicted on the basis of the mole percentage of deuterium in the sample. One possible explanation for the lower than expected deuterium signal is contamination of the PCl_3 by environmental water either during the transfer to the sample or on storage prior to use. It was determined that contamination was not the source of this discrepancy when

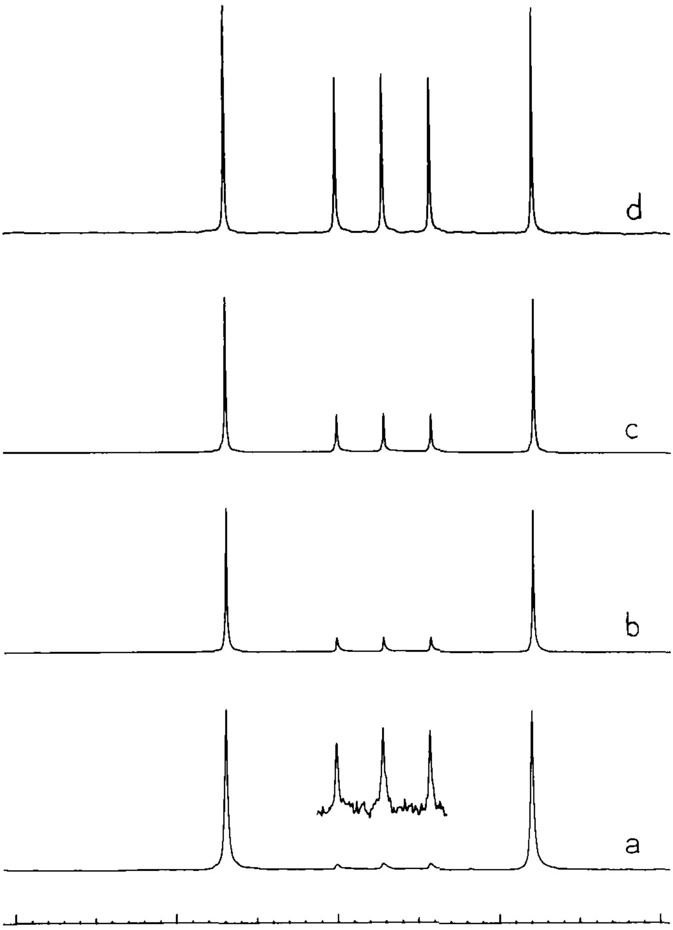

Figure 1. ^{31}P Spectra of Phophorous Acid Solutions at Various Degrees of Deuteration. A: 18.3%; B: 37.6%; C: 57.5%; D: 77.4%

no observable proton doublet was observed after reaction with 100.0% deuterium oxide (Aldrich). It was determined also that the cause of the reduced deuterium signal was not a longer relaxation time for the deuterated sample when spectra acquired with pulse delays of 10, 100 and 400 seconds had no differences in the relative proton to deuteron intensities outside of normal exper-

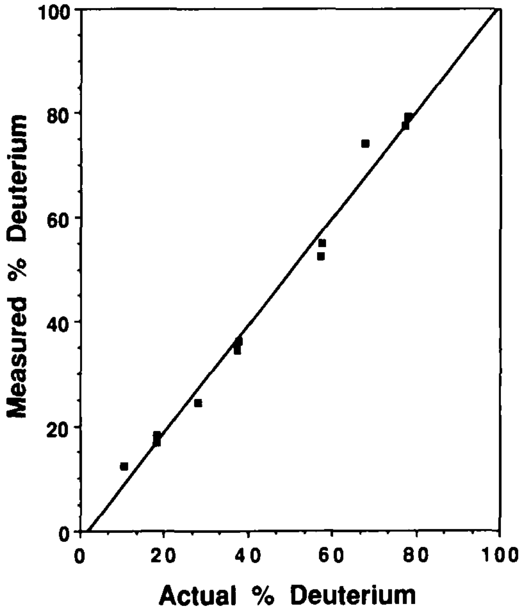

Figure 2. Measured Deuteration Percent versus Actual Deuteration Percent. Measured percent calculated from Equation 3.

imental error (approximately ± 5%). Therefore, a 10 second pulse delay was used to acquire all of the data reported here.

In order to explain the lower than expected signal strength for the deuterated compound, the data were analyzed assuming that an isotope effect favored reaction by proton over deuterium. It was found that the data could be well explained by an isotope effect that favors reaction with proton over reaction with deuteron by a factor of 3.2 ± .25 (95% C.I.). It is interesting to note that an isotope effect of 3.1 was measured by Salomaa et. al. for the ionization of weak acids.[5]

Figure 2 shows a plot of the percentage deuterium calculated from the experimental spectra, corrected for a 3.2 isotope effect, versus the actual mole percent of deuterium in the sample. The experimental percentage of deuterium was calculated from the relative integrated intensities of the deuterium and protium signals in the following way:

$$R = \frac{k_D C_D}{k_H C_H} \qquad (1)$$

Where R is the ratio of integrated intensities ($^2H/^1H$), C_H is the actual proton concentration of the sample, C_D is the actual deuterium concentration, k_H is the rate constant for reaction with proton and k_D is the rate constant for reaction with deuterium.

Rearranging equation 1 and assuming that $C_H + C_D = 110$ M leads to equation 2 for the concentration of deuterium. Dividing equation 2 by 110 ($C_H + C_D$), assigning a value 3.2 to the k_H/k_D ratio and expressing as a percentage leads to equation 3 from which the mole percentage of deuterium in a sample can be calculated from the measured ratio of deuterium to proton integrals. The data summarized in Figure 2 were generated by using equation 3 to convert the measured integrals to deuterium percentages. These deuterium percentages are plotted versus the deuterium mole percent calculated from the weights of deuterium oxide and water used to make each sample.

$$C_D = \frac{110Rk_H/k_D}{1 + Rk_H/k_D} \qquad (2)$$

$$\text{Deuteration } \% = \frac{320R}{1 + 3.2R} \qquad (3)$$

The linear regression line drawn in Figure 2 has a slope of 1.03 and a Y intercept of -1.8% with a correlation coefficient of 0.993. The average error between the measured and actual deuterium percentages is 6.6% relative. This experimental error is comparable to the typical error involved in the measurement of integrals and indicates that the source of error probably lies in the data acquisition rather than in the chemical system.

Although this technique was only tested on aqueous solutions, it is, in principle, applicable to any protic solvent system (e.g. alcohols) that produces phosphite ion upon reaction with PCl_3.[6] It is, of course, very possible that a different isotope effect will be operative in other solvents. Although the hydrolysis of PCl_3 was used to produce the phosphite ion in this work, one could, obviously, utilize other phosphorus (III) halides or other compounds (e.g. P_4O_6) that produce phosphite when reacted with the desired solvent. With the easy availability of multinuclear Fourier Transform NMR spectrometers, this technique is one that can be quickly and easily performed in most reasonably equiped laboratories.

Aknowldedgment: This work was supported by the UNO Research Council.

REFERENCES

1. Goldman, M., Arch. Sci. (Geneva) 1957, 10, 247-249

2. Paulsen, P. J.; Cooke, W. D. Anal. Chem. 1964, 36, 1713-1721

3. Gomez, G. V. Junta Energ. Nucl. (Spain) 1975, 302-313

4. Leyden, D. E.; Reilley, C. N. Anal. Chem. 1965, 37, 1333-1338

5. Salomaa, P.; Schaleger, L. L.; Long, F. A. J. Am. Chem. Soc. 1964, 86, 1-7

6. Emsley, J.; Hall, D. "The Chemistry of Phosphorus", Harper & Row, London, 1976.

Date Received: 01/18/89
Date Accepted: 02/27/89