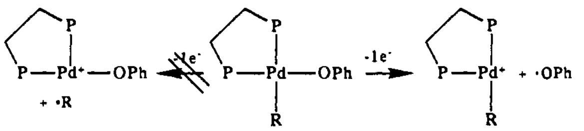
firmed these to be irreversible one-electron oxidation processes similar to the palladium–dialkyls. These potentials are given in Table I. The results qualitatively confirm the relative bond strength predictions for late metal–oxygen and late metal–carbon bonds.[19] It also shows that oxidative homolysis is not necessarily restricted to metal–alkyl bonds.



(3)

Conclusions

The reductive elimination of alkanes from palladium–dialkyl complexes is a well-established reaction pathway.[20] These reactions are usually achieved thermally and are believed to proceed by a mechanism involving ligand dissociation. Furthermore, palladium bis(phosphine) complexes are commonly used as catalysts for coupling two alkyl groups.[2] Oxidative processes were also known to induced reductive elimination of R–R, as has been reported for $[(bpy)_2Fe^{IV}R_2]^{2+}$ formed by the oxidation of $[(bpy)_2Fe^{III}R_2]^{+}$.[21] Therefore, the one-electron oxidative cleavage of palladium–alkyl bonds was an unforseen result.

Oxidative cleavage of zirconium–alkyl bonds is more easily rationalized. Zirconium(IV) has no d electrons, and only the bonding electrons of the ligands are available to be removed by oxidation. In PdR_2L_2 systems there are eight accessible nonbonding d electrons. Though related palladium(IV) compounds are known,[22] none were observed in these experiments. In all cases examined, the one-electron oxidation of palladium(II)–dialkyls and alkylphenoxides results in retention of the d^8 configuration of palladium(II). As in the zirconium(IV) case, only the predominantly bonding electrons of the ligands are involved in the net oxidation reactions. This contrasts with results obtained by Kochi et al. for the iron–alkyl systems where all the oxidations were reported to be metal based.[21] It is worth noting that the zirconium and palladium complexes are both even spin state systems (d^0, d^8 square planar), which exhibit similar oxidation chemistry and expulsion of an alkyl radical from an odd-electron intermediate. The $[(bpy)_2Fe^{III}R_2]^+$ intermediate complex, which chemically decomposes to yield an alkyl radical species,[21] is also of odd spin state (d^5 high spin). Only the even-electron $[(bpy)_2Fe^{IV}R_2]^{2+}$, produced by oxidation, undergoes reductive elimination to R–R. Whether this correlation with net spin is a general trend merits further study. A caveat is the possibility of efficient R–R coupling by attack of $R^\bullet$ on the M–R bond of a labile complex, as appears possible in the palladium systems when no trapping ligand is present.

The oxidation of zirconium- and palladium–alkyl complexes yields highly reactive metal complexes. The $[Cp_2ZrR]^+$ species has proven to be an effective ethylene polymerization catalyst.[4,5] The reactivity of $[(L_2)PdR]^+$ has not yet been fully explored. Several transition metal nitrile complexes are active nitrile hydration catalysts.[23] Late metal alkoxides and aryloxides have also been proposed as models for olefin hydration.[9] Carbon monoxide insertion into metal–carbon and other heteroatom bonds is another reaction proposed frequently in catalytic reactions.[1,2] Studies of the reactivity types discussed above are currently underway with these $[(L_2)PdR]^+$ reactive species.

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Direct Determination of Equilibrium Deuterium Isotope Effects at Natural Abundance

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Abstract: A great variety of techniques has been used to study deuterium–protium partitioning in exchanging systems at equilibrium. In this context it is shown that the determination of site-specific isotope contents by ^{2}H-NMR at natural abundance provides simple and direct access to thermodynamic isotope fractionation factors. This method avoids the recourse to deuterated species and therefore the approximations inherent in the analysis of complex isotopomeric mixtures. A number of slowly exchanging systems involving OH, NH, or SH groups and water offer suitable conditions (large chemical shift differences, moderate line widths, ...) for the relatively accurate determination of thermodynamic fractionation factors. Moreover multiple fractionations can be observed and compared in ternary mixtures.

Knowledge of the thermodynanic fractionation factors in exchanging systems at equilibrium is of considerable interest for interpreting chemical or biochemical mechanisms. In this respect, hydrogen isotope exchange processes between water and exchangeable groups (OH, NH, SH, ...) occur frequently in biological media. A great deal of effort has been devoted to the determination of the equilibrium partitioning of deuterium and protium using a wide variety of experimental[1-13] and theoretical[14] methods. The experimental determinations require the use of

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labeled compounds, and most of them do not provide direct access to the isotopic equilibrium constants. Various investigations of hydro–alcoholic systems have exploited a combination of independent mass spectrometry measurements of the isotope separation factors between hydrogen gas and liquid water or liquid alcohol.[1] Other determinations have been performed by vapor pressure,[2] calorimetric,[3] distillation–density,[4] and infrared[5,6] techniques. NMR methods have also been applied to the study of thermodynamic isotope effects in systems exchanging either slowly or rapidly with respect to the NMR time scale.[6-12] Fractionation factors can thus be obtained by monitoring the proton NMR chemical shift of the exchanging nuclei, referred to an external reference, as a function of the NMR fraction of solute either in light or in heavy water of known deuterium content.[7-10] Accurate referencing of the average proton chemical shift is obtained by using the deuterium lock of the NMR spectrometer.[11] Another interesting approach exploits the existence of deuterium isotope effects on the ^{13}C chemical shifts of labeled molecules. The isotope equilibrium constants associated with one or several rapidly exchanging groups can thus be obtained by using concentric tubes to measure the chemical shift differences between dilute solutions in H_2O and D_2O or in H_2O and D_2O–H_2O mixtures.[12] In conditions of slow exchange in deuterium-enriched media, the various deuterated isotopomers are observed separately on the ^{13}C spectrum, and the deuterium/protium ratios at a given molecular site can be obtained from the integrated intensities.[13] Although a preference of deuterium for the alcoholic species is now recognized in the case of hydro–alcoholic mixtures for instance, the results derived from the various methods are relatively scattered.

We have shown that ^2H-NMR at natural abundance is the source of powerful methods to appraise and quantify isotope fractionation intervening in the course of chemical and biochemical mechanisms.[15] In particular, access to site-specific natural isotope fractionation by NMR (SNIF-NMR) has recently been the basis for a new approach to the determination of equilibrium liquid–vapor fractionation factors.[16] In this report it is shown that the isotopic equilibrium constants of slowly exchanging systems in the liquid state are easily accessible with good accuracy by the ^2H-NMR method. This direct method can also provide simultaneous access to multiple fractionation factors. Moreover, in contrast with all other methods, it has the advantage of avoiding recourse to deuterium-enriched media, a source of complex isotopomeric mixtures when equivalent exchangeable hydrogens are present.

Table I. Deuterium–Protium Isotope Fractionation in Exchange Equilibria Involving OH, NH, or SH Groups and Water[a]

mixtures	partners	$\Delta\nu$ (Hz)	n	α (σ)
1-propanol–water	PrOH–H_2O	43.6	7	1.15 (0.02)
2-propanol–water	iPrOH–H_2O	45.0	10	1.13 (0.03)
2-propanol–methanol	iPrOH–MeOH	8.2	13	1.03 (0.03)
2-propanol–water–methanol	iPrOH–H_2O	22	13	1.10 (0.03)
	MeOH–H_2O	14.7	13	1.17 (0.03)
	iPrOH–MeOH	7.3	13	0.95 (0.04)
2-methyl-1-propanol–water	iBuOH–H_2O	36.5	6	1.11 (0.02)
2-butanol–water	sBuOH–H_2O	34.9	13	1.08 (0.03)
3-methyl-1-butanol–water	ROH–H_2O	46.4	6	1.17 (0.04)
methyl salicylate–ethanol	ROH–EtOH	374.7	6	0.94 (0.02)
2-mercaptoethanol	SH–OH	−88.2	4	0.41 (0.01)
N-methylacetamide–water	–NH–H_2O	107.4	5	1.18 (0.01)

[a] $\Delta\nu$ is the deuterium chemical shift difference between the signals of the exchanging nuclei in hertz at 61.4 MHz (302 K). The value of the fractionation factor, α, (eq 1) is the mean over n independent determinations. Although the number of experiments is sometimes only 4 to 6, standard deviations, σ, have been computed in all cases.

Table II. Thermodynamic Isotope Fractionation Factor, α, Associated with Hydrogen Exchange between the Hydroxyl Site of Ethanol and Water at Different Concentrations[a]

water content (% w/w)	n	$\Delta\nu_{1/2}$ (Hz)		$\frac{S_{\mathrm{ROD}}}{S_{\mathrm{HOD}}}$ (σ)	α	$(\mathrm{D/H})^{\mathrm{A}}_{\mathrm{III}}$ (ppm)	$(\mathrm{D/H})^{\mathrm{w}}$ (ppm)
		ROD	HOD				
15.32	7	5.44	5.28	1.179 (0.008)	1.09	150.0	137.8
12.66	8	4.51	4.86	1.465 (0.016)	1.08	148.0	136.7
10.07	7	4.30	4.67	1.864 (0.026)	1.07	145.7	136.1
7.64	7	3.44	3.42	2.597 (0.016)	1.10	144.9	132.2
6.90	7	3.62	4.26	2.839 (0.048)	1.07	143.4	133.7
5.37	7	3.63[b]	4.33[b]	3.540 (0.190)	1.03	140.7	137.2
5.02	7	3.60[b]	4.80[b]	3.865 (0.087)	1.04	140.3	135.2

[a] n is the number of spectra run successively. $\Delta\nu_{1/2}$ is the half-height line width of the deuterium NMR signal. $S_{\mathrm{ROD}}/S_{\mathrm{HOD}}$ is the ratio of the signal areas and σ is the standard deviation. The site-specific isotope contents in the hydroxyl site of ethanol, $(\mathrm{D/H})^{\mathrm{A}}_{\mathrm{III}}$, and in water, $(\mathrm{D/H})^{\mathrm{w}}$, have been computed from the overall isotope ratio over these two sites, $(\overline{\mathrm{D/H}})$, using the corresponding experimental value of α. $(\overline{\mathrm{D/H}})$ was itself calculated from the isotope ratios measured in pure ethanol, $(\mathrm{D/H})_{\mathrm{III}} = 136.1$ ppm, and in the added water, $(\mathrm{D/H})^{\mathrm{w}} = 152.8$ ppm. The mean values of the site-specific isotope ratios of the methyl (I) and methylene (II) sites of ethanol, determined (eq 3) in two series of 8 successive experiments are $(\mathrm{D/H})_{\mathrm{I}} = 100.4$ ppm and $(\mathrm{D/H})_{\mathrm{II}} = 126.2$ ppm. [b] The free induction decay has been subjected to an exponential multiplication associated with a line-broadening factor of 0.2 Hz.

Experimental Section

Materials. All chemicals were of analytical reagent grade. Water was freshly distilled. The components were weighed on a high-precision balance. In most cases mole fraction a was controlled with good accuracy (±0.03%) by Karl Fischer titration. C_6F_6 ($\simeq 8$ g L^{-1}) was added to every sample for NMR field-frequency locking.

NMR Determinations. The NMR spectra were recorded on Bruker WH-250 or WM-400 instruments. The WM-400 spectrometer is equipped with a probe specially designed for deuterium observation and a ^{19}F field-frequency locking device. The ^2H longitudinal relaxation times, T_1 of the methyl (I), methylene (II), and hydroxyl (III) isotopomers of ethanol, in a 96%/4% v/v ethanol–water mixture, were measured by the inversion–recovery method, and the corresponding transverse relaxation times, T_2, were determined by the Hahn sequence.[17a]

site	I	II	III	n
T_1 (s)	1.05 (0.05)	1.15 (0.05)	0.13 (0.005)	9
T_2 (s)	1.00 (0.15)	1.20 (0.15)		3
$\Delta\nu_{1/2}$ (Hz)	0.75 (0.05)	0.65 (0.05)	3.35	5

n is the number of experiments and $\Delta\nu_{1/2}$ the half-height line width. The

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standard deviations are given in parentheses.

Since ^{2}H relaxation is relatively slow, high values of the acquisition time (At ≥ 6.8 s) were selected in order to ensure complete relaxation between successive pulses. The ^{2}H spectra were obtained in the presence of broad band proton decoupling, but it was checked that the nuclear Overhauser effect did not significantly influence the quantitative determinations.

Signal to noise ratios higher than 100 must be ensured, and phase adjustments must be carefully performed.[18] Six to eight spectra were run successively for every sample. The signal areas were determined by Lorentzian curve fitting using dedicated software.

The isotope ratios of the three sites of the pure ethanol sample (99.957%) selected as a starting material for the experiments described in Table II have been determined by an intermolecular referencing procedure (eq 3) using tetramethylurea as a working standard. The isotope content of the added water was obtained by isotope ratio mass spectrometry.

Methods and Results

At natural abundance, only the monodeuterated isotopomers are involved in the exchange equilibria and the site-specific isotope ratios, $(D/H)_i$, defined as the ratios of the numbers of deuterium and protium atoms in sites i, can be directly determined from ^{2}H-NMR spectra obtained in quantitative conditions.[19] When two sites i and j of molecules AH and BH, containing P_i^A and P_j^B exchangeable protons, respectively, are engaged in a reaction of type I, the thermodynamic fractionation factor,[20] $\alpha^{A/B}$, and the equilibrium constant $K^{A/B}$ are related by eq 1.

$$\mathrm{AH} + \mathrm{BD} \overset{K^{A/B}}{\rightleftharpoons} \mathrm{AD} + \mathrm{BH} \qquad \text{(I)}$$

$$\alpha^{A/B} = \frac{(D/H)_i^A}{(D/H)_j^B} = \frac{P_j^B}{P_i^A} K^{A/B} \qquad (1)$$

In the dilute isotopic conditions at natural abundance, $\alpha^{A/B}$ may be computed simply from the ratios of the AD and BD signal areas in the deuterium spectrum and from the mole fractions a and $1 - a$ of compounds AH and BH in the mixture

$$\alpha^{A/B} = \frac{P_j^B}{P_i^A} \frac{S_{AD}}{S_{BD}} \frac{1-a}{a} \qquad (2)$$

More generally the site-specific isotope ratios of compounds A and B, either isolated or mixed, are accessible from appropriate NMR referencing procedures.[18] Thus the integrated intensity of a given signal, k, can be compared to that of a working standard, WS, (such as tetramethylurea) with a precisely known deuterium content, $(D/H)^{WS}$. The isotope ratio associated with site k of A for instance is obtained from the signal areas S^{WS} of WS and S_k^A of k in the deuterium spectrum of A or of the A–B mixture

$$\left(\frac{D}{H}\right)_k = \frac{S_k^A}{S^{WS}} \frac{P^{WS}}{P_k^A} \frac{m^{WS}}{m^A} \frac{M^A}{M^{WS}} \left(\frac{D}{H}\right)^{WS} \qquad (3)$$

P, m, and M are respectively the stoichiometric number of hydrogens in the considered position, the weight, and the molecular weight of A or WS.

Alternatively the $(D/H)_k^{A-B}$ ratios can be obtained from combined measurements of the overall isotope contents $\overline{(D/H)}^{A-B}$ of compounds A and B by isotope ratio mass spectrometry and of the molar fractions, f_k, of the monodeuterated isotopomers by ^{2}H-NMR.

$$(D/H)_k = \frac{f_k}{F_k}\overline{(D/H)} \qquad (4)$$

F_k is the statistical mole fraction of isotopomer k. The isotope ratios of the exchanging sites i and j in a mixture can be calculated from their independent values measured in the precursors and from the $\alpha^{A/B}$ value obtained from eq 2.

Since accurate values of the molar fractions a, are readily accessible, the accuracy of the results is mainly conditioned by that of the signal area determinations in the ^{2}H spectra.[19] Relatively favorable conditions are frequently ensured by large differences in the resonance frequencies (Table I) and moderate line widths. The standard deviation in the area ratios resulting from iterative curve fitting performed on 10 spectra of the 2-propanol–water mixture, for example, is better than 0.03.

It should be emphasized that the present approach avoids the problems which occur in enriched media due to the presence of multilabeled species. In such media it is necessary, in particular, to consider equilibria of types II and III and to take into account the large deviation of the equilibrium constant K^W with respect to the statistical value 4

$$2\mathrm{ROH} + \mathrm{D_2O} \overset{K'}{\rightleftharpoons} 2\mathrm{ROD} + \mathrm{H_2O} \qquad \text{(II)}$$

$$\mathrm{H_2O} + \mathrm{D_2O} \overset{K^W}{\rightleftharpoons} 2\mathrm{HDO} \qquad \text{(III)}$$

Moreover all other possible isotopic equilibria involving exchangeable sites with several equivalent positions (such as NH_2) must then be considered. In contrast only monodeuterated molecules, HDO or ROD, significantly contribute at the natural abundance level, and hydrogen isotope exchange in water–alcohol mixtures is therefore simply described by eq 1 where $K^{A/B}$ can be expressed as a function of the equilibrium constants K' and K^W of equilibria II and III by

$$K^{A/B} = (K'/K^W)^{1/2} \qquad (5)$$

In order for the method to be used to determine $\alpha^{A/B}$, the exchange reaction between partners A and B must be sufficiently slow on the NMR time scale. The suitability of the exchange rate can first be checked by observing the OH and H_2O proton resonance line shapes and taking into account the significant lowering in the coalescence temperature expected at the deuterium resonance frequency.[18] For a better appraisal of this phenomenon, we have investigated a freshly distilled 96%/4% v/v mixture of ethanol and water. Both ^{1}H and ^{2}H coalescence figures were observed in variable temperature experiments performed at a constant field associated with resonance frequencies of 250 and 38.5 MHz, respectively. Line separations of 200 Hz for ^{1}H and 30.5 Hz for ^{2}H were derived from the behavior of the hydroxyl and water chemical shifts in the slow exchange limit. Coalescence was observed at 360 K in the proton spectrum and at 320 K in the deuterium spectrum. The lifetimes at the coalescence temperatures, calculated[17b] by total line shape analysis of the figures resulting from exchange between two unequally populated sites, were $\tau_c = 0.04$ s for ^{1}H and $\tau_c = 0.03$ s for ^{2}H. The rates of exchange at room temperature being frequently situated in the vicinity of the NMR sensitive time domain, not all ranges of water concentrations may be appropriate to the determination of α. Contamination by small amounts of acid or base which catalyze the exchanges[21] must be avoided since only one averaged signal is then observed. Moreover line broadening occurring at intermediate exchange rates is detrimental to the accuracy of the area measurements. In such cases signal narrowing can be obtained by slightly lowering the temperature. In practice slow exchange figures with ^{2}H line widths less than 5 Hz are frequently encountered for mixtures involving carefully purified samples of alcohols, water, thiols, amides, etc. The fractionation factors determined for a variety of equilibria involving not only alcohol–water or alcohol–alcohol mixtures but also the SH–OH partners of 2-mercaptoethanol or the NH–H_2O hydrogens of an N-methylacetamide–water mixture are given in Table I. In each case the number, n, of experiments is at least 4.

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(20) The term "isotope fractionation factor" frequently defines the isotope content of a given site A with respect to that of water. Here, $\alpha^{A/B}$ compares, more generally, the relative isotope affinity for site A and for an exchanging partner B. The fractionation factor of A with respect to water can be derived from $\alpha^{A/B}$ and the fractionation factor of B with respect to water.

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Since changes in the hydrogen-bonded structures of hydroalcoholic media may occur as a function of the relative proportions of the partners, we have investigated the ethanol–water system in more detail. The values of the isotope fractionation factor, α, and of the site-specific isotope contents in the hydroxyl site of ethanol, $(D/H)_{III}$, and in water, $(D/H)^{W}$, have been determined at seven water concentrations (Table II).

Discussion

Most investigations of isotopic equilibria involving the OH group are concerned with water and methanol. The equilibrium constant $K^{A/B}$ for an exchange of type I in which AH is methanol and BH is water has been determined by a variety of experimental methods. The following values reported in chronological order illustrate the dispersion of the results (at 248 K unless otherwise stated): 0.500 and 0.481 ± 0.015 (at 353 K) (distillation–density measurements[4]); 0.46 ± 0.02 (infrared spectroscopy[5]); 0.50 ± 0.03 (proton NMR[9b]); 0.6 ± 0.1 (calorimetry[3a]); 0.454 (semiempirical calculations[14b]); 0.56 ± 0.02 (liquid–vapor exchanges[1d]); 0.54–0.58 (statistical mechanics[14c]); 0.53 ± 0.01 (vapor pressure measurements[2a,b] and eq 5 with $K^{W} = 3.85$[8b]); 0.54 ± 0.02 (separation factor between hydrogen gas and aqueous methanol mixtures: mass spectrometry[1c]); 0.53 (at 308 K) (^{13}C NMR[12]). In the case of ethanol–water mixtures, an equilibrium constant $K^{A/B} = 0.522$ is indirectly derived from the experimental values for equilibria III and II: $K^{W} = 3.85$[1c,14a] and $K' = 1.05 \pm 0.02$ (obtained at 298 K by vapor pressure measurements[2c]). A value $K^{W} = 3.94$[8c] would lead to $K^{A/B} = 0.516$. A preference of deuterium for the hydroxyl site of the alcohol is recognized in the most recent experimental and theoretical determinations, however fractionation factors α very close to unity or even smaller have been measured in certain alcohol–water mixtures.[9b,12] Our results, obtained on different linear or branched alcohols (Table I), provide direct and unambiguous evidence of the higher affinity of ^{2}H for the alcohol than for the water. Nevertheless more strongly associated groups such as the intramolecularly hydrogen-bonded hydroxyl of methyl salicylate are characterized by reduced deuterium affinity. The deuterium–protium partitioning in the *N*-methylacetamide–water system also results in a noticeable imbalance of ^{2}H in favor of the nitrogen site. The measured fractionation factor is in reasonable agreement with two other literature values[11,12] $\alpha = 1.12$ and $\alpha = 1.16$. The low isotopic equilibrium constant characterizing the exchange between the SH and OH groups of 2-mercaptoethanol is also in line with the strong discrimination against deuterium occurring in thiols as compared to water.[13,22,23]

In addition the method can also be used to compare several fractionation factors directly. It is shown that appropriate ternary mixtures involving water and two different alcohols enable three fractionation parameters to be simultaneously obtained. In particular the fractionation factors between 2-propanol and water and between 2-propanol and methanol can be determined either in the ternary system 2-propanol–methanol–water or independently in the binary mixtures 2-propanol–water and 2-propanol–methanol. In addition, by resorting to ternary mixtures, it may be possible to measure fractionation parameters, such as that of the methanol/water equilibrium, which are inaccessible in the binary system due to fast exchange.

Strong variations in the hydrogen-bonded structures formed by the alcohol and water molecules are likely to occur as a function of the relative concentration. In this respect several alcohol–water mixtures have been shown to exhibit particular behavior, such as minima and maxima at relatively low concentrations, either of alcohol or of water.[24,25] In principle, intermolecular effects may also exert an influence on the ratios of the reduced isotopic partition functions of the exchanging species which govern the equilibrium isotope fractionation effects. In fact, when comparing the values of the fractionation factor measured at seven concentrations of water in ethanol (Table II), no systematic variation in the α parameter is detected, at the experimental accuracy of the results, for mole fractions of alcohol increasing from 0.68 to 0.84. A mean value $\alpha = 1.08$ is computed over the five concentrations situated in this range. Significantly lower values of α are measured at mole fractions 0.87–0.88. This behavior may be paralleled for instance with that of the excess heat capacity at constant volume which exhibits a peak at a mole fraction of ethanol higher than 0.8.[25] However, it should be noted that at increasing dilutions of one of the partners, the signal area measurements of the minor component suffer from a progressive loss in accuracy.

A reliable estimation of the isotopic equilibrium constants is of prime importance in investigations of all media where exchange reactions may intervene. Due to the lack of consistent values of $K^{A/B}$, it is frequently more or less explicitly assumed that a change in the isotope content of the solvent produces identical partitioning in the exchanging sites of the solute. However, such rough approximations may be the source of relatively strong discrepancies in the analyses of fractionation effects. Some attention has been given to the ethanol–water system, which constitutes a powerful probe for inferring the isotopic behavior of carbohydrate precursors. Owing to the site-specific dimension introduced by the ^{2}H-NMR method (SNIF-NMR[15]) a detailed appraisal of the molecular isotope distributions at natural abundance has become possible, and the isotope ratios in the methyl (I) and methylene (II) sites of ethanol for instance (Table II) are easily accessible. Precise knowledge of the thermodynamic fractionation factor relating the isotope contents of water and of the ethanol hydroxyl in a fermentation medium then enables a proper interpretation of the isotopic balance even in conditions where the exchange is fast on the NMR time scale.[15c] The whole set of isotope ratios associated with the starting ethanol and water partners and their mixtures (Table II) illustrate the strong isotopic redistribution which may operate in such exchanging media.

Finally, it is worth pointing out that the present method may also provide simultaneous access to primary and all secondary thermodynamic isotope effects in tautomeric equilibria. Work is in progress to exploit this attractive potential.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 2-methyl-1-propanol, 78-83-1; 2-butanol, 78-92-2; 3-methyl-1-butanol, 123-51-3; methyl salicylate, 119-36-8; 2-mercaptoethanol, 60-24-2; *N*-methylacetamide, 79-16-3.

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