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A NMR method for the analysis of mixtures of alkanes with different deuterium substitutions

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Abstract

^{13}C NMR at 125.76 MHz with ^{1}H and ^{2}H decoupling, ^{2}H NMR at 76.77 MHz with ^{1}H decoupling, and ^{1}H NMR at 500.14 MHz with ^{2}H decoupling were employed as analytical tools to study the complex mixtures of deuterated ethanes resulting from the catalytic H–D exchange of normal ethane with gas-phase deuterium in the presence of a platinum foil. Reference samples consisting of 1:1 binary mixtures of pure normal ethane and ethane-d$_n$ ($n = 1–6$) were used to identify the peak positions in the ^{13}C, ^{2}H, and ^{1}H NMR spectra due to each individual isotopomer, and the effect of isotopic substitution on the chemical shifts was determined in each case. While the NMR of all three nuclei worked well for the identification of the individual components of the 1:1 standard mixtures, both ^{1}H and ^{2}H NMR suffered from inadequate resolution when studying complex reaction mixtures because of the broadening of the lines due to ^{1}H–^{1}H (^{1}H NMR) and ^{2}H–^{2}H (^{2}H NMR) couplings. ^{13}C NMR was therefore determined to be the method of choice for the quantitative analysis of the reaction mixtures. Using the ^{13}C NMR results, a correlation that takes into account the primary and secondary isotope substitution effects on chemical shifts was deduced. This equation was used for the identification of the individual components of the mixtures, and integration of the individual observed resonances was then employed for quantification of their composition. This study shows that ^{13}C NMR with ^{1}H and ^{2}H decoupling is a viable procedure for studying mixtures of deuterated ethanes. Furthermore, the additivity of the isotopic effects on chemical shifts and the transferability of the values obtained with ethane to other molecules makes this approach general for the analysis of other isotopomer mixtures. © 1997 Elsevier Science B.V.

Keywords: NMR; Ethane mixtures; Isotopic substitution; H–D exchange; Catalysis

1. Introduction

In this work the feasibility of using nuclear magnetic resonance (NMR) spectroscopy as an analytical technique to quantitatively analyze mixtures of deuterated alkanes was evaluated. The analysis of such mixtures is in general quite difficult, because it is not only important to consider the number of hydrogen atoms being substituted by deuteriums, but also their specific position within the molecules. This is particularly relevant in catalysis, where detailed information

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on the positions where H–D exchange takes place can be directly related to the mechanism involved in that process [1,2]. Here we use a prototypical system, the reaction mixture obtained by the catalytic exchange of normal ethane with deuterium over a platinum foil [3–6], to test the usefulness of NMR in this endeavor. The specific goal of this research was to spectroscopically quantify the amounts of symmetric and asymmetric deuterated compound present in the final gas mixture, in particular those for ethane-d_2. In a second paper we will address the use of mass spectrometry for the same purpose [7].

Little research has been reported so far on the NMR of deuterated alkanes. Early NMR studies on the effect of isotope substitutions on chemical shift, reviewed by Batiz-Hernandez and Bernheim in 1967 [8], indicated that the sign of the isotope shift is almost always negative, that is, the resonance frequencies decrease (move upfield) with heavy isotope substitution (although there are a few exceptions to this rule [9]). In addition, the magnitude of the isotope shift has been found to be a function of the resonant nucleus, being higher for nuclei with larger chemical shift ranges (i.e. ^{13}C has a larger chemical shift range than either ^{1}H or ^{2}H, and therefore incurs greater chemical shift differences upon isotopic substitution than those observed in the corresponding ^{1}H and ^{2}H spectra). In addition, the magnitude of the isotope-induced shift depends on: (1) the remoteness of the isotopic substitution site from the observed nucleus; (2) the fractional change in mass; and (3) the number of atoms substituted by isotopes. With regard to the latter point, it appears that the intrinsic NMR isotope effects are approximately additive, that is, that each isotopic substitution acts almost independently of the others, and that the overall shift observed in the NMR spectra of a particular atomic center comes out to be close to the sum of all possible contributions [10–12]. As an example of this, it has been reported that $CH_{4-n}D_n$ mixtures ($n = 0$–4) yield both ^{1}H [13] and ^{13}C NMR [14] spectra with approximately equally-spaced peaks, and other systems have shown similar behavior too [15–19].

Here, the correlation between NMR chemical shifts and isotopic substitutions was studied by using the ^{1}H- and ^{2}H-decoupled ^{13}C NMR spectra of several mixtures of deuterium-substituted ethanes of known compositions. Two types of isotope effects on chemical shift were observed, as expected: (1) a primary isotope effect for deuterium substitution on the ^{13}C nucleus under observation ($^1\Delta^{13}$C); and (2) a secondary isotope effect when the deuterium substitution takes place on the carbon adjacent to the ^{13}C nucleus under observation ($^2\Delta^{13}$C). The additivity rules were found to apply to this system not only when the isotopic substitution occurs on only one of the two ethane carbons (for instance, in the $CH_3{}^{13}CH_{3-n}D_n$ molecules, where $n = 1$–3), but also in cases where substitutions were made on a site different than that under measurement (as in $CH_{3-n}D_n{}^{13}CH_2D$, $CH_{3-n}D_n{}^{13}CHD_2$, or $CH_{3-n}D_n{}^{13}CD_3$). The data obtained with these controlled experiments were then successfully applied to the analysis of several complex mixtures obtained from catalytic exchange studies. Finally, primary isotope effects were also determined on ^{1}H-decoupled ^{2}H NMR and ^{2}H-decoupled ^{1}H NMR spectra, and the results of the three methods were compared.

2. Experimental section

All NMR data were collected at 25°C on a General Electric GN-500 NMR spectrometer equipped with a home-built X-nucleus decoupler and a Z-spec 5 mm inverse-detection broad-band probe. ^{1}H NMR spectra were collected as 16k complex data points with an operating frequency of 500.1357 MHz and a sweep width of 6536 Hz; this sets the digital error for the chemical shifts at ± 0.0008 ppm. Typically sixteen transients were acquired and averaged for each spectrum. ^{1}H NMR spectra with ^{2}H decoupling (CW) were acquired in a similar manner except that the X-nucleus decoupler was set to the ^{2}H resonance frequency of $C_2{}^2H_6$ (76.7725 MHz) and gated on during data acquisition. ^{2}H NMR spectra were collected as 16k complex data points with an operating frequency of 76.7738 MHz and a sweep width of 615 Hz (chemical shift digital precision $= \pm 0.0005$ ppm). Typically 32 transients were acquired and averaged for each spectrum. ^{2}H NMR spectra with ^{1}H decoupling (500.1357 MHz, standard phase modulated) were acquired in a similar manner except for the fact that the ^{1}H decoupler was gated on during the data acquisition. ^{13}C NMR spectra were collected as above, but with an operating frequency of 125.763 MHz and a sweep width of 11364 Hz (chemical shift digital precision = ± 0.006 ppm), and transients were acquired and averaged until acceptable signal to noise levels were obtained. ^{1}H- and ^{2}H-decoupled ^{13}C NMR spectra were obtained in the same way, but the ^{1}H and ^{2}H decoupling channels were again gated on during data acquisition. The flip angle was set at 45°, and delay times of 60 s were used for quantitative analysis and of 3 s otherwise (see later). All ^{2}H NMR spectra and those requiring ^{2}H decoupling were collected in the unlocked mode. Spectral data were transferred to a Silicon Graphics Personal Iris 4D35 computer and processed using Felix (Biosym Technologies).

^{1}H, ^{2}H, and ^{13}C NMR spectra were recorded for pure normal ethane (C_2H_6, Matheson, 99.9%) and for each of the following deuterated ethanes (Merck-Canada and CIL, 99% atom purity): CH_3CH_2D, CH_3CHD_2, CH_2DCHD_2, CH_3CD_3, CH_2DCD_3, CHD_2CHD_2, CHD_2CD_3 and C_2D_6. A second set of spectra were taken for 1:1 mixtures of $C_2H_6 + CH_3CH_2D$, $C_2H_6 + CH_3CHD_2$, $C_2H_6 + CH_2DCHD_2$, $C_2H_6 + CH_3CD_3$, $C_2H_6 + CH_2DCD_3$, $C_2H_6 + CHD_2CHD_2$ and $C_2D_6 + CHD_2CD_3$. Finally, a third set of NMR measurements were performed for the following samples: (1) an equimolar mixture of all the ethane molecules available to us (those listed above, nine in total); and (2) several mixtures of deuterated ethanes obtained via the catalytic hydrogen-deuterium exchange of normal ethane, as described below. In one instance $^{13}CH_3CH_3$ (CIL, 99% isotopic purity) was used in the latter case in order to increase the signal-to-noise ratio of the ^{13}C NMR spectrum. The spectrum of pure $^{13}CH_3CH_3$ was also taken for reference.

All the NMR samples were prepared by first premixing the gases in a stainless steel recirculating loop reactor system described in detail in a previous publication [4] and then freezing them into a 5 mm o.d. Pyrex NMR tube filled with 0.5 ml of deuterated chloroform (Aldrich, 99.9% atom D). The NMR tube was directly attached to a larger glass tube equipped with a stopcock valve and connected to the reaction system. The trapping procedure for the reference binary mixtures was as follows: (1) the whole reactor, including the arm to which the NMR tube was connected, was pumped to the mTorr range with a mechanical pump; (2) 10 Torr of each of the gas samples was introduced individually into the reaction system while maintaining the stopcock of the NMR tube closed; (3) that valve was opened to allow for the gas mixture to condense into the liquid nitrogen-cooled NMR tube; and (4) the valve was then closed and the tube flame-sealed. The same procedure was employed for the multicomponent mixtures, except that 5 Torr of each of the gases was used for mixtures containing more than two components. The NMR signals of the deuterated chloroform ($CDCl_3$) were employed as reference for the chemical shift scales by assuming values of 7.26 and 77 ppm for the ^{2}H and ^{13}C peaks, respectively. The small peak due to normal chloroform ($CHCl_3$) impurities seen in the ^{1}H NMR spectra was also set at 7.26 ppm.

Finally, several reaction mixtures of deuterated ethanes were obtained by catalytic hydrogen-deuterium exchange between normal ethane and deuterium over a platinum foil (Aldrich, 99.99% purity) 0.1 mm thick and of 1.12 cm^2 total area [4]. 50 Torr of either normal C_2H_6 or C_2H_6-1-^{13}C and 500 Torr of D_2 were introduced in the microbatch reactor and allowed to mix for approximately 5 min with the recirculating pump, and the foil was then heated to a constant temperature (to 625 K in the two cases reported here). The reactions were followed mass spectrometrically by continuously leaking the gas mixture into a computer-interfaced Dycor MA-200M quadrupole mass spectrometer linked to the circulating loop system, and stopped after a preset overall conversion was reached (approximately 20% for the ^{13}C-enriched mixture and 50% for the unenriched one). The mixtures were then condensed into the NMR tube, the excess deuterium gas was pumped away, and the tubes were sealed as described before.

3. Results

3.1. ^{13}C Nuclear magnetic resonance

The complete assignment of the ^{13}C NMR resonances from the mixtures of deuterated ethanes was achieved by comparison with spectra from the pure substances. The resonances for all of the deuterated ethanes were measured with both ^{1}H and ^{2}H decoupling to simplify the spectra, and lie in the range between 6.7 and 5.5 ppm. The NMR shift for the majority of the deuterated pure standards (CH_3CH_2D, CH_3CHD_2, CH_3CD_3, CH_2DCHD_2, CHD_2CHD_2 and CH_2DCD_3) were obtained in 1:1 mixtures with C_2H_6, while that for CHD_2CD_3 was measured in the presence of an equal amount of C_2D_6. In order to simplify the following discussion, substitutions of hydrogens by deuteriums on the methyl moiety under measurement, the one with the carbon atom which we will call primary, will be named α-substitutions, while isotopic substitutions on the neighboring methyl fragment, that of the secondary carbon, will be called β-substitutions. As examples of these determinations, Fig. 1 shows the spectra of CD_3CHD_2 and CH_3CH_2D mixed with C_2D_6 and C_2H_6 respectively. Under the ^{13}C NMR measurement conditions used here (^{1}H and ^{2}H decoupling), only one and two resonance are observed for C_2H_6 and CH_3CH_2D, respectively: the resonance at 6.700 ppm corresponds to C_2H_6, and those at 6.410 and 6.600 ppm to $CH_3{}^{13}CH_2D$ and $^{13}CH_3CH_2D$, respectively. From this, the measured isotope shift due to one deuterium atom α-substituted in ethane-d_1, $CH_3{}^{13}CH_2D$, was found to be $^{1}\Delta^{13}C = -290$ ppb, while the isotope shift experienced by the secondary carbon in $^{13}CH_3CH_2D$ due to the influence of the same deuterium atom (in this case β-substituted) was $^{2}\Delta^{13}C = -100$ ppb. The spectrum of CD_3CHD_2 mixed with C_2D_6 shows three resonances as well: one at 5.530 ppm which corresponds to C_2D_6, and two at 5.820 and 5.630 ppm from $CD_3{}^{13}CHD_2$ and $^{13}CD_3CHD_2$, respectively. Again, the isotope shifts resulting from substituting one normal hydrogen for a deuterium atom in the α and β positions of ethane-d_5 relative to the resonance frequency of C_2D_6 were calculated to be -290 and -100 ppb.

Fig. 2 shows the ^{13}C NMR spectra of CH_3CHD_2, CH_2DCHD_2 and CH_2DCD_3, each in a 1:1 mixture with normal ethane. The chemical shifts for these compounds, two for each, were found to be 6.499 and 6.119 ppm for $^{13}CH_3CHD_2$ and $CH_3{}^{13}CHD_2$, 6.210 and 6.020 ppm for $^{13}CH_2DCHD_2$ and $CH_2D^{13}CHD_2$, and 6.106 and 5.726 for $^{13}CH_2DCD_3$ and $CH_2D^{13}CD_3$, in that order. From this, the isotope shift from substituting two α-deuteriums in CH_3CHD_2 was determined to be -581 ppb, or -290.5 ppb per deuterium, while the influence of two β-substituted deuteriums came out to be -201 ppb, or -100.5 ppb per deuterium. The isotope shifts of -680 and -490 ppb for ethane-1,2,2-d_3 are the result of the influence of either two α-substituted plus one β-substituted deuterium (two times -290 ppb plus one time -100 ppb) or one α-substituted plus two β-substituted deuteriums (one time -290 ppb plus two times -100 ppb), depending on the carbon atom being probed. Finally, the asymmetric ethane-1,2,2,2-d_4 shows isotope shifts of -974 and -594 ppb, which are the result of the combined effect of three α-substituted plus one β-substituted deuterium for one

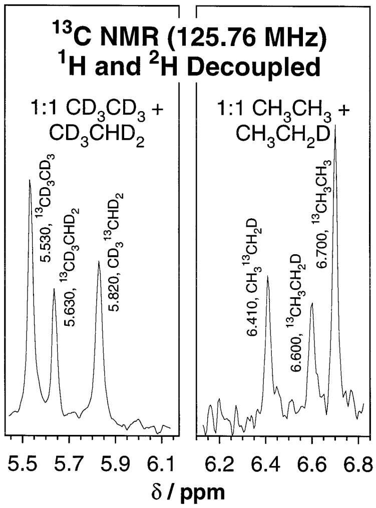

Fig. 1. Representative ^{1}H- and ^{2}H-decoupled ^{13}C NMR spectra from the 1:1 mixtures used in the calibration of the chemical shifts induced by deuterium substitution. The left panel shows the trace for an equimolar mixture of CD_3CD_3 and CD_3CHD_2, while the right frame presents the data for the $CH_3CH_3 + CH_3CH_2D$ combination.

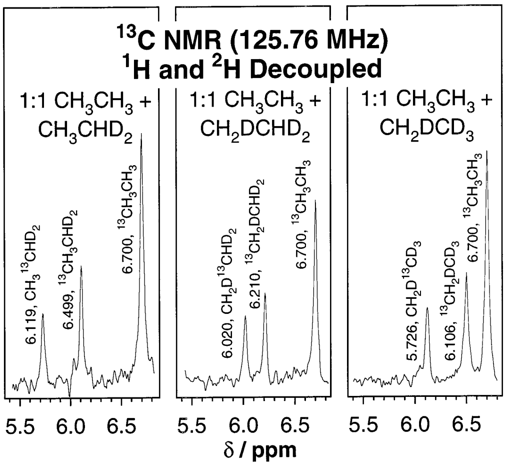

Fig. 2. Additional ^{1}H- and ^{2}H-decoupled ^{13}C NMR for 1:1 mixtures of CH_3CH_3 with one other pure ethane isotopomer: CH_3CHD_2 (left panel), CH_2DCHD_2 (center panel), and CH_2DCD_3 (right panel). A summary of the data obtained with mixtures such as these is given in Table 1.

carbon and of one α-substituted plus three β-substituted deuteriums for the other. This series of ^{13}C NMR reference spectra was completed by measuring the chemical shifts for CH_3CD_3 and CHD_2CHD_2 (spectra not shown). The whole data set is summarized in Table 1.

The main conclusion from these experiments is that the effect of each deuterium substitution on the chemical shifts in the ^{13}C NMR spectra of deuterated ethanes is independent of any other substitutions, and that therefore the additivity rule applies well to this system. Indeed, the data provided here show that the isotope shifts that originate from any single α- or β-substitution amount to about $^{1}\Delta^{13}C = -290$ ppb and $^{2}\Delta^{13}C = -100$ ppb, respectively, as measured directly on the ethane-d_1 sample, and that all of them add up to induce the overall observed displacements. The general equation to calculate the chemical shifts $\delta^{13}C$ seen in the ^{13}C NMR spectra of each deuterated ethane is:

$$\begin{aligned}
&\delta^{13}C(C_2H_{6-x}D_x)\\
&= \delta^{13}C(C_2H_6) + (^{1}\Delta^{13}C \cdot n_{\alpha\text{-D}} + {}^{2}\Delta^{13}C \cdot n_{\beta\text{-D}})\\
&\Delta^{13}C = \delta^{13}C(C_2H_{6-x}D_x) - \delta^{13}C(C_2H_6)\\
&\quad = -(0.290 \cdot n_{\alpha\text{-D}} + 0.100 \cdot n_{\beta\text{-D}}\ (\text{ppm}) \qquad (1)
\end{aligned}$$

where $n_{\alpha\text{-D}}$ and $n_{\beta\text{-D}}$ are the number of α- and β-deuterium substitutions in the ethane isotopomer being considered. Normally each compound yields two peaks in the ^{13}C NMR spectrum, one for each carbon (the definitions for the α and β positions are relative to the carbon atom being probed, and therefore reverse when switching atoms), but in the symmetric molecules (CH_3CH_3, CH_2DCH_2D, CHD_2CHD_2, and CD_3CD_3) the two signals are identical and collapse into one single feature. The accuracy of Eq. (1) is greater than ± 4 ppb, as estimated by comparing the measured and calculated values for the shifts in Table 1.

The reference data obtained with the experiments reported above was then used to analyze the composition of mixtures of deuterated ethanes obtained after the catalytic H–D exchange reactions described in the experimental section [4]. Fig. 3 displays the NMR spectra obtained for two of those mixtures, one collected after a 20% conversion in the H–D exchange of ^{13}C-enriched perhydrido-ethane ($^{13}CH_3CH_3$) with deuterium (left), and another prepared by 50% conversion of normal (unenriched, CH_3CH_3) ethane. It can be seen from that figure that the chemical shifts observed for each of the components in the mixtures compare very well with those of the standards, never deviating by more than ± 3 ppb (see Table 2, [4]). Notice in particular that the resolution of the resonances in the mixtures was sufficient to allow for the identification of all the species present. This is especially important in catalytic experiments such as these, where the most interesting species from the point of view of mechanistic determinations (the ethane-d_2 species in this case) are only present in small amounts (see below).

The quantitative analysis of the ^{13}C NMR spectra for the ethane mixtures is complicated by the long T_1 relaxation times of the carbon nucleus [20]. As a consequence, long relaxation delay times must be used during data collection in order to prevent signal saturation and to insure that the areas of the integrated resonances truly reflect the concentration of the corresponding nuclei. With the goal of evaluating the magnitude of this effect in the analysis of our ethane mixtures, ^{13}C NMR

Table 1
^{13}C NMR chemical shifts ($\delta^{13}C$) for individual deuterated ethanes

Structure	$\delta^{13}C$ (ppm)	Isotope shift $\Delta^{13}C$ (ppb) (relative to C_2H_6)		
		Experimental	Calculated	Difference
$^{13}CH_3CH_3$	6.700	0	0	0
$^{13}CH_3CH_2D$	6.600	−100	−100	0
$CH_3\,^{13}CH_2D$	6.410	−290	−290	0
$^{13}CH_3CHD_2$	6.499	−201	−200	−1
$CH_3\,^{13}CHD_2$	6.119	−581	−580	−1
$^{13}CH_2DCH_2D$	—	—	−390	—
$^{13}CH_3CD_3$	6.403	−297	−300	3
$CH_3\,^{13}CD_3$	5.828	−872	−870	−2
$^{13}CH_2DCHD_2$	6.210	−490	−490	0
$CH_2D^{13}CHD_2$	6.020	−680	−680	0
$^{13}CH_2DCD_3$	6.106	−594	−590	−4
$CH_2D^{13}CD_3$	5.726	−974	−970	−4
$^{13}CHD_2CHD_2$	5.919	−781	−780	−1
$^{13}CHD_2CD_3$	5.820	−880	−880	0
$CHD_2\,^{13}CD_3$	5.630	−1070	−1070	0
$^{13}CD_3CD_3$	5.530	−1170	−1170	0

The calculated isotope shifts were obtained by using Eq. (1). Digital precision in chemical shifts = ±0.006 ppm.

spectra were acquired for the 1:1 $C_2H_6+CH_3CD_3$ mixture by using relaxation delays of 60 and 3 s (data not shown). The integrated relative areas for the three peaks obtained in both cases are listed in Table 3. It can be seen there that while the areas in the spectrum recorded with the three second delay deviate significantly from those expected based on both the one-to-one ratio of ^{13}C atoms in CH_3CD_3 (because of the expected equal concentrations of $^{13}CH_3CD_3$ and $CH_3\,^{13}CD_3$) and the one-to-one ratio in the concentrations of C_2H_6 and CH_3CD_3 in the mixture, the data obtained with sixty second delays approach the theoretical values. Unfortunately, increasing the delay time between pulses increases the data collection time accordingly (the 60 s between-pulses spectrum mentioned above required about six hours of data acquisition time). As a consequence, while it is in principle possible to use the natural abundance of ^{13}C in normal samples to determine their composition by ^{13}C NMR, this may sometimes not be practical because of the lengthy data acquisition times required to obtain reasonable signal-to-noise ratios. This is the reason why ^{13}C-enriched ethane was used in one of the H–D exchange catalytic experiments (Fig. 3, left [4]): the delay time between pulses could then be increased and acceptable signal-to-noise levels could still be reached without using prohibitively long data acquisition times. Nevertheless, the data from the experiments with normal (unenriched) samples indicate that those are still quite feasible (see below). The 60 s delay times used to acquire the data in Table 1 were estimated to induce a systematic error in the concentration estimates of about 10% towards lower values.

All ^{13}C NMR data were collected with the ^1H and ^2H decouplers off during the relaxation delay

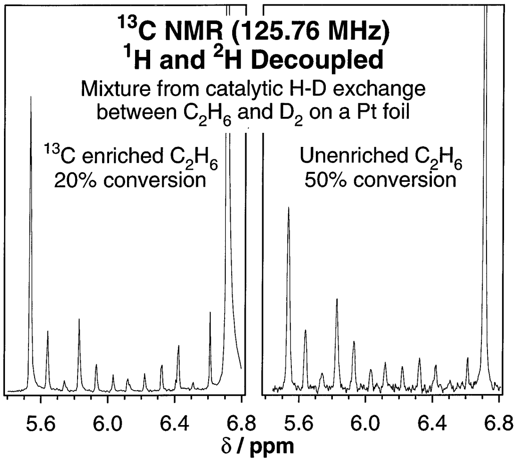

Fig. 3. ^{1}H- and ^{2}H-decoupled ^{13}C NMR spectra for two mixtures of deuterium-substituted ethanes obtained by H–D exchange reactions of normal (d_0) ethane with deuterium over a platinum catalyst. Left: mixture obtained with ^{13}C-enriched ethane after a 20% conversion. Right: mixture obtained with natural abundance ^{13}C-ethane after a 50% conversion. The reaction conditions in both cases were initial C_2H_6 and D_2 pressures of 50 and 500 Torr, respectively, and a reaction temperature of 625 K.

to eliminate nuclear Overhouser effects (NOE), a common problem in ^{13}C NMR; they were gated on only during the acquisition of the free induction decay (FID). The spectra in Fig. 3 were then baseline corrected, and the peak signals were integrated in order to evaluate the relative contributions of each component in the mixture. The composition of the mixtures obtained this way agree quite well with those estimated independently by low-resolution mass spectrometry, even for samples where unenriched ethane was used (Table 2, [4]), but additional information (not available from the mass spectrometric analysis) was obtained with the NMR data regarding the relative amounts of symmetrically- and asymmetrically-substituted isotopomers with the same number of deuterium substitutions. There are some differences between the results from both techniques, but those may be not only due to the underestimation of the concentration of the highly deuterium-substituted species because of the short delay times between pulses used, but also to the deconvolution technique used in the analysis of the low-resolution mass spectrometry data [4,7]. It is important to highlight here that even though the use of ^{13}C-enriched samples may make the data analysis easier and more accurate, normal unenriched samples do yield reasonable results as well (see for instance the spectrum in the right panel of Fig. 3). Moreover, several experimental protocols can be used to improve the quantification of the ^{13}C NMR signals, including the use of relaxation agents in the mixture or specific pulse sequences during the NMR spectra acquisition [20].

Table 2
^{13}C NMR and low resolution mass spectrometric analysis of a sample consisting of a mixture of deuterated ethanes, obtained after 10 min of reaction between 50 Torr of C_2H_6 and 500 Torr of D_2 over a platinum foil heated to 625 K. The NMR spectra is shown in the right panel of Fig. 3.

Compound	$\delta\,^{13}$C (ppm)	Concentration (% total)	
		^{13}C NMR	Low Res. MS
CH_3CH_3	6.698	53.9	43.0
CH_3CH_2D	6.601, 6.410	4.9	13.3
CH_3CHD_2	6.501, 6.110	1.1	5.3
CH_2DCH_2D	6.311	1.9	
CH_3CD_3	6.400, 5.828	0	3.4
CH_2DCHD_2	6.207, 6.019	3.5	
CH_2DCD_3	6.107, 5.729	3.4	5.2
CHD_2CHD_2	5.920	3.8	
CHD_2CD_3	5.818, 5.627	12.2	11.3
CD_3CD_3	5.523	15.3	18.5

Table 3
Comparison of signal intensities (peak areas) between ^{13}C NMR spectra of deuterated ethane mixtures taken with different delay times between pulses. The sample probed consisted of a 1:1 mixture of CH_3CH_3 and CH_3CD_3

Compound	$\delta\,^{13}$C (ppm)	Relative signal intensity		
		3 s delay	60 s delay	Expected
$^{13}CH_3CH_3$	6.700	1.00	1.00	1.00
$^{13}CH_3CD_3$	6.403	0.38	0.45	0.50
$CH_3\,^{13}CD_3$	5.828	0.22	0.43	0.50

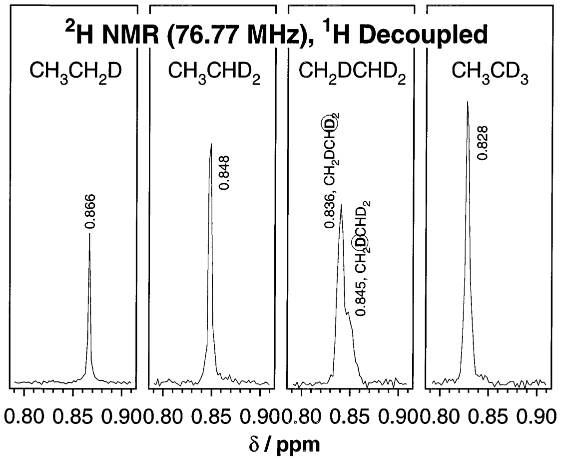

Fig. 4. ${}^1H$-decoupled ${}^2H$ NMR of four pure ethane isotopomers. From left to right, those compounds are: CH_3CH_2D, CH_3CHD_2, CH_2DCHD_2, and CH_3CD_3. The chemical shifts obtained by experiments such as these with all the pure isotopomers available to us are summarized in Table 4.

3.2. ${}^2H$ Nuclear magnetic resonance

${}^2H$ NMR spectra for each deuterium-substituted ethane were recorded as well. All ${}^2H$ NMR measurements were done with ${}^1H$ decoupling to avoid the presence of multiplets due to H–D couplings. The signals for the reference mixtures appear in the range $\delta^2H = 0.866\text{-}0.800$ ppm, the limits corresponding to monodeutero- and perdeutero-ethane respectively, while those for the H–D exchange reaction sample were slightly displaced to the $\delta^2H = 0.870–0.806$ ppm range.

A similar analysis to that used for the ${}^{13}C$ NMR spectra can be used here for the ${}^2H$ NMR data. To begin with, Fig. 4 compares the ${}^2H$ NMR resonance frequencies for CH_3CH_2D, CH_3CHD_2 and CH_3CD_3, the ethane isotopomers that have deuteriums in only one of the carbon atoms and therefore give rise to one single resonance each. The observed chemical shifts, δ^2H, decrease as the number of deuteron substituents on the ethane molecule increases, from 0.866 ppm for CH_3CH_2D to 0.848 ppm for CH_3CHD_2 and 0.828 ppm for CH_3CD_3. From this, the isotope shift $\Delta^2H = \delta^2H\ (CH_3CHD_2) - \delta^2H\ (CH_3CH_2D)$ due to the α-substitution of one hydrogen by deuterium on the monodeuteroethane molecule was found to be -18 ppb, and a second α-substitution on the resulting dideuteroethane-1,1-d_2 cause an additional isotope shift $\Delta^2H = \delta^2H\ (CH_3CD_3)\text{-}\delta^2H\ (CH_3CHD_2)$ of about -20 ppb; the average comes out to be an isotope shift of ${}^1\Delta^2H = -19$ ppb per α-substituted deuterium. Next, the chemical shifts of CH_2DCHD_2 and CH_3CHD_2 are also contrasted in Fig. 4. There are two distinct types of deuteriums in CH_2DCHD_2, and consequently two (not completely resolved) resonances are seen in that case at 0.836 and 0.845 ppm, with relative intensities of approximately 2:1: the peak at 0.836 ppm belongs to the $-CHD_2$ deuteriums and is the result of one α and one β substitution, while the signal at 0.845 ppm belongs to the $-CH_2D$ deuterium and shifts because of the influence of two β substitutions. Notice that the signal of the $-CHD_2$ group in CH_2DCHD_2 is shifted by about $\Delta^2H = -12$ ppb with respect to that for CH_3CHD_2, an effect associated with one β-substitution; analysis of other samples provides a value for that effect closer to ${}^2\Delta^2H = -9$ ppb.

Additional measurements were done with all the other reference compounds available. Table 4 summarizes the ${}^2H$ NMR parameters for each of the individual deuterated ethanes. As mentioned above, the individual shifts upon α- and β-isotope substitutions were estimated to be about ${}^1\Delta^2H = -19$ ppb and ${}^2\Delta^2H = -9$ ppb, respectively, and were shown to also be additive. From this the following equation was derived to determine the chemical shifts for each species present in the mixture of deuterated ethanes:

$$\begin{aligned}
&\delta^2H(C_2H_{6-x}D_x)\\
&= \delta^2H(C_2H_5D) + ({}^1\Delta^2H \cdot n_{\alpha\text{-D}} + {}^2\Delta^2H \cdot n_{\beta\text{-D}})\\
&\Delta^2H = \delta^2H(C_2H_{6-x}D_x) - \delta^2H(C_2H_5D)\\
&\quad = -(0.019 \cdot n_{\alpha\text{-D}} + 0.009 \cdot n_{\beta\text{-D}})\ (\text{ppm}) \qquad (2)
\end{aligned}$$

The shifts calculated using this equation are also reported in Table 4.

Inspection of Table 4 points to one of the shortcomings of using ${}^2H$ NMR for the analysis of mixtures of deuterium isotopomers. It can be seen there that the absolute errors incurred in calculating the chemical shifts for unknown sam-

Table 4
^{2}H NMR chemical shifts (δ^2H) for individual deuterated ethanes. The calculated isotope shifts were obtained by using Eq. (2). Digital precision in chemical shifts = ±0.0005 ppm.

Structure	δ^2H (ppm)	# D atoms		Isotope shift Δ^2H (ppb)		
		α-carbon	β-carbon	Experimental	Calculated	Difference
CH_3CH_2D	0.866			0	0	0
CH_2DCH_2D	—	0	1	—	−9	—
CH_3CHD_2	0.848	1	0	−18	−19	1
CH_2DCHD_2	0.845	0	2	−21	−18	−3
	0.836	1	1	−30	−28	−2
CH_3CD_3	0.828	2	0	−38	−38	0
CH_2DCD_3	0.838	0	3	−28	−27	−1
	0.816	2	1	−50	−47	−3
CHD_2CHD_2	0.829	1	2	−37	−37	0
CHD_2CD_3	0.816	1	3	−50	−46	−4
	0.810	2	2	−56	−56	0
CD_3CD_3	0.800	2	3	−66	−65	−1

ples by using Eq. (2) are about the same as in the case of the ^{13}C NMR, but that the relative errors are much larger because the absolute shifts induced by deuterium substitutions are more than an order of magnitude smaller in the ^{2}H NMR case: the worst cases in Table 1 display differences between the experimental and calculated chemical shifts of less than 1%, while those in Table 4 can show discrepancies of the order of 10%. In addition, there are many overlaps in the ^{2}H NMR spectra, a problem compounded by the low resolution of the individual peaks. For instance, the signals for the asymmetric ethane-d$_4$ overlap with those for CH_2DCHD_2 and ethane-d$_5$, and one of the peaks for CH_2DCHD_2 is close to that for the asymmetric ethane-d$_2$.

In order to further test the analytical power of ^{2}H NMR for the quantitative analysis of isotopomeric samples, a spectrum was taken for an equimolar mixture of all the deuterated ethanes used in this work (all possible isotopomers except for the symmetric ethane-d$_2$). The left panel of Fig. 5 shows that spectrum, which displays about ten distinguishable resonances. The end resonances at 0.869 and 0.805 ppm clearly correspond to ethane-d$_1$ and ethane-d$_6$, respectively. Also, using the data from the reference spectra (Table 4), the peak at 0.814 ppm can be easily assigned to the $-CD_3$ deuteriums of ethane-d$_5$. The identification of the rest is somewhat hindered by the overlap of many of the features in the spectrum, but the data is nevertheless of good enough quality to render individual peaks for almost all unequivalent deuteriums, allowing for the complete identification of all compounds in the equimolar

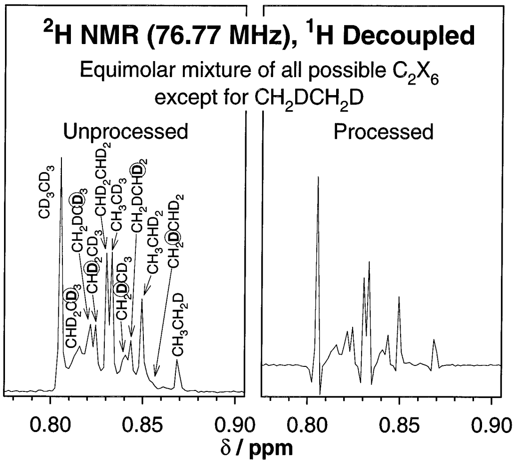

Fig. 5. ^{1}H-decoupled ^{2}H NMR spectra for an equimolar mixture of all possible ethane isotopomers except for the symmetrically-substituted ethane-d$_2$ (CH_2DCH_2D). Left: raw data and peak assignment. Right: spectra obtained by using a double exponential window function before Fourier transformation of the time-based data, as described by Brown et al. [23]. The peak assignment and relative peak areas are also provided in Table 5.

Table 5
^2H NMR chemical shifts and relative intensities for an equimolar mixture of all possible deuterated ethanes except for ethane-1,2-d_2.

Structure	$\delta\,^2H$ (ppm)		Relative intensities	
	Experimental	Calculated	Experimental	Expected
CH_3CH_2D	0.869	0.869 (reference)	1.0	1
CH_3CHD_2	0.850	0.850	2.3	2
CH_2DCHD_2	0.851	0.851	0.6	1
	0.843	0.841	1.3	2
CH_3CD_3	0.833	0.831	3.8	3
CH_2DCD_3	0.840	0.842	1.5	1
	0.821	0.822	2.3	3
CHD_2CHD_2	0.830	0.832	2.7	4
CHD_2CD_3	0.824	0.823	1.4	2
	0.814	0.813	4.5	3
CD_3CD_3	0.805	0.804	4.4	6

mixture; Table 5 contrasts the chemical shifts observed experimentally with those calculated using the formula provided above. This is however no longer true in the case of the mixtures that results from the catalytic studies, because in those systems the concentration of some of the isotopomers is too low to be well resolved in the ^2H NMR spectra (Fig. 6).

It can also be seen from the example above that even though the effect of deuterium substitution on the chemical shift appears to be additive, there is insufficient resolution to adequately quantify most mixtures (see the comparison between the experimental and calculated ^2H NMR peak areas in Table 5). It is in principle possible to improve the resolution of the spectra by using zero filling and resolution-enhancement approaches in which the accumulated decay signal is multiplied by a weighting function before the Fourier transformation of the data [21,22]. A direct comparison with the approach described by Brown et al. [23] was done here by using a double exponential weighting function on the data from the equimolar ethane mixture, the result of which is displayed in the right panel of Fig. 5. The results of that analysis show that in practice this procedure distorts the peak shapes and renders the quantitative analysis unreliable. Alternatively, the raw spectra could be fitted to a set of Lorentzian peaks. This was also attempted for the equimolar mixture used in Fig. 5, but even though the overall fit was quite good, the individual areas obtained this way displayed rather large errors (see Table 5). It is worth mentioning that the original data appears to reflect the composition of the mixture quantitatively since, after normalizing the total area of the spectrum to the 28 deuterium atoms expected from the mixture, the area of the peak for CH_3CH_2D (the only one clearly separated from the rest) amounted to the expected value of one (the actual experimental value was 1.004). The failure of the fitting analysis in yielding an accu-

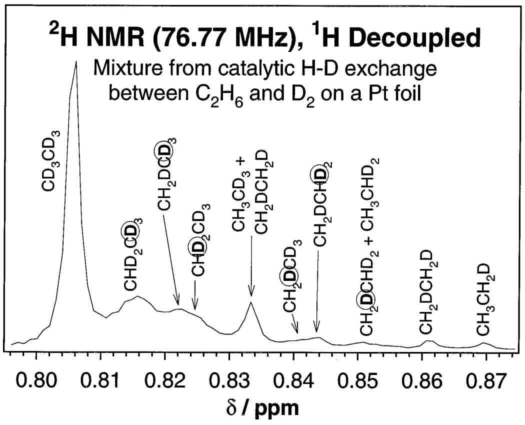

Fig. 6. ^1H-decoupled ^2H NMR spectrum for the reaction mixture obtained after catalytic exchange of normal C_2H_6 with D_2 over a platinum foil. This is the same sample as in the left panel of Fig. 3. The assignment of the peaks to the different isotopomers is also provided.

rate estimate of the composition of the sample is most likely due to the fact that the shapes for the ^{2}H NMR peaks of the three species which have two types of unequivalent deuterium atoms may be dominated by unresolved deuterium–deuterium couplings. Overall, ^{2}H NMR proved to be adequate for the identification of the components of complex ethane mixtures, but not good enough to obtain quantitative information about their composition.

3.3. ^{1}H Nuclear magnetic resonance

In a further attempt to identify and quantify the composition of complex mixtures of deuterated ethanes, proton NMR was also employed in this study. As in the ^{13}C and ^{2}H NMR characterization, ^{1}H NMR spectra of 1:1 mixtures of ethane with the various deuterated ethanes were run first. The normal non-decoupled spectra displayed only broad and nondescript multiplets. The spectra were simplified significantly by employing ^{2}H decoupling, but still presented complex multiplets due to $^{1}H-^{1}H$ coupling for all but CH_3CD_3, CHD_2CD_3 and CHD_2CHD_2, which collapsed to single resonances. It would be normally expected for the ^{2}H-decoupled ^{1}H NMR spectra of the deuterated ethanes to collapse to multiplets containing no more than four peaks, but that is not the case; higher-order splittings appear here because the chemical shift differences between the coupled protons is of the same order as the coupling constant for these same protons. Therefore, while it is possible to partially identify the chemical shifts and coupling constants for the 1:1 ethane reference mixtures used in this work, it is much more difficult to analyze mixtures of deuterated ethanes, especially those resulting from H–D exchange reactions. To illustrates the degree of difficulty of this task, Fig. 7 shows the spectrum obtained for the equimolar mixture used before, together with a partial assignment of the peaks. The ^{1}H NMR spectra could be simplified somewhat by running them on a higher field instrument, but that would not completely eliminate the many overlapping resonances expected for the mixture. As the objective here is to analyze complex mixtures of deuterated ethanes quantitatively, ^{1}H NMR can be deemed unsatisfactory.

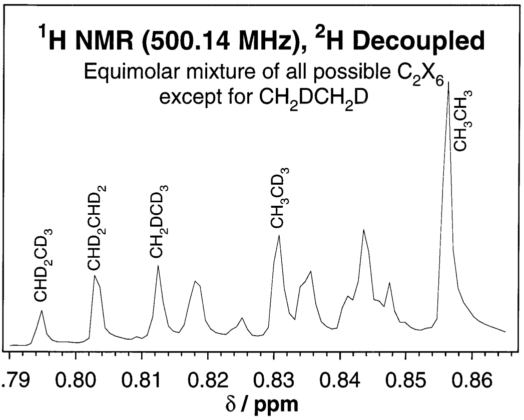

Fig. 7. ^{2}H-decoupled ^{1}H NMR spectrum of the equimolar mixture of ethane isotopomers used in the experiment reported in Fig. 5. A partial peak identification was attempted, but the complete assignment was hindered by the splitting of the signals for hydrogens in asymmetric ethane molecules due to $^{1}H-^{1}H$ spin couplings.

4. Discussion

The main goal of this research was to develop a reliable method for the analysis of mixtures of isotopomers of hydrocarbons, in particular of ethane. In our evaluation of NMR as a technique to be used for this task, a few general observations were made. First, examining the results obtained by ^{13}C, ^{2}H and ^{1}H NMR, it was found that deuterium isotope substitutions always induce upfield chemical shifts in the signals, as reported before [8]. Also, this effect was proven to be greater on ^{13}C than the other nuclei, most likely because of the correspondingly greater chemical shift range in the ^{13}C NMR. Third, it was shown that ^{1}H- and ^{2}H-decoupling in the ^{13}C NMR spectra gives rise to simple spectra for each deuterated compound. The effect of deuterium substitution on the ethane chemical shift was directly correlated with the number of deuterium substituents and the positions occupied by each deuterium in the ethane molecule. Thus, two isotope effects were observed: (1) $^{1}\Delta^{13}C$, the effect observed when the deuterium substituted is bonded to the nucleus under observation; and (2) $^{2}\Delta^{13}C$, the effect observed when the substituted deuterium is one carbon away from the nucleus under observation. The value for $^1\Delta^{13}C$ was found to be -290 ppb per deuterium, quite close to those reported by Wesener et al. for monodeuterated ethane (-284 ppb), propane (-299 ppb), and ethyl benzene (-296 ppb) [10], suggesting that these values are transferable to other compounds. In addition, the value of $^2\Delta^{13}C$ was found to be -100 ppb per deuterium, and both effects were found to be additive.

The large separation in the ^{13}C NMR spectra among the signals from the different isotopomers of ethane and the additive nature of the effect of isotopic substitution on chemical shifts make this technique ideal for the analysis of isotopomeric mixtures. In particular, it was shown here that it is clearly possible to distinguish between symmetrically and asymmetrically substituted ethanes. This turned out to be key in the determination of the mechanism involved in the H/D exchange of ethane over platinum catalysts [4]. In particular, it was found that the yield for CH_2DCH_2D production was more than twice that for CH_3CHD_2, a result that suggests that adsorbed ethylene is one of the main intermediates in the mechanism for the complete exchange of normal ethane to the perdeutero isotopomer [1,3,4].

It is also worth noticing that a particular challenge in the analysis of mixtures of isotopomers from catalytic processes is the fact that the several products are produced in significantly different quantities. First of all, it is desirable to keep the overall conversion low in order to avoid significant contributions from secondary reactions, which means that a large fraction of the mixture is still composed of the reactants (more than 50% of the mixtures analyzed here was C_2H_6). In addition, the particular system studied in this work favors either mono- or per-deutero substitutions; the concentrations of CH_3CH_2D and CD_3CD_3 in the sample reported in Table 2 were about 13 and 19%, respectively. The challenge was to determine the ratio of symmetric to asymmetric ethane-d$_2$ produced from a total of about 5% $C_2H_4D_2$ in a complex matrix, and ^{13}C NMR did a nice job of it. As shown above, quantification of NMR signals is easily accomplished by integration of the observed ^{13}C resonances, and is accurate to within a few percent provided that the spectra are acquired employing a sufficient relaxation time. The overall composition obtained with NMR matched reasonably well that from mass the spectrometry analysis [4,7].

It has also been shown here that ^2H NMR can in principle be used in a similar manner to analyze mixtures of deuterated ethanes. However, even though a resolution enhancement routine and an increased field as compared with that in the report by Brown et al. [23] were used in this work, the resolution was still insufficient to accurately quantify the composition of the mixture. In order to obtain a complete separation of the signals in the deuterium spectra peak fitting needed to be employed, and that procedure proved unreliable as well. Consequently, ^2H NMR is obviously a less desirable technique than ^{13}C NMR for these analyses, even though ^2H NMR does have the advantage that it is more sensitive than ^{13}C NMR and therefore requires less acquisition time, especially if ^{13}C unenriched samples are used. Finally, proton NMR suffers from the complications of second order splittings, which causes severe overlap of the observed resonances. Fitting theses types of spectra is in principle possible, but requires knowledge of the exact chemical shifts and $^1H-^1H$ coupling constants.

It should be straightforward to extend the analytical approach reported here to the study of more complex systems. In particular, it would be useful to extend the work on platinum to other metals, since different catalysts display different exchange patterns: while some only favor single exchange steps, others catalyze complete exchange exclusively, and a third group (which includes platinum) is capable of promoting both pathways [5]. It would also be interesting to study the H-D exchange in larger alkanes, starting with either propene or neopentane, for which a new mechanistic channel involving α, γ-diadsorbed intermediates is open. It would be expected for the values of the isotope-induced chemical shifts measured in this work to be applicable to those problems.

5. Conclusions

The use of NMR was evaluated as an analytical method to study a complex mixture of deuterated ethanes. The results indicate that the isotope substitution effects on ethane chemical shifts are additive and can therefore be predicted by using a general simple equation, thus allowing for the identification of each individual deuterated ethane in complex mixtures. The power of this NMR approach is that not only the degree but also the regiospecificity of deuterium substitution can be easily extracted from the data. ^{13}C NMR (^{1}H and ^{2}H decoupled) proved particularly powerful for the analysis of isotopomer mixtures, and lead to the first complete determination of the composition of mixtures resulting from H-D catalytic exchange processes, including the relative presence of all symmetrically and asymmetrically deuterated compounds. It was also shown that ^{2}H NMR (^{1}H decoupled) can be used for this purpose, but with less confidence, as the resolution is insufficient to allow for accurate quantification. Resolution enhancement via data processing was proven to provide only slight improvements in the ^{2}H NMR case, and to possibly introduce some artifacts. Finally, ^{1}H NMR was shown to suffer from complications induced by overlapping multiplets due to $^{1}H-^{1}H$ coupling, which makes it unreliable for the study of deuterated ethanes. Of the three nuclei available for NMR in the study reported here, ^{13}C was shown to be by far the best choice because of the superior resolution and degree of simplicity in the spectra obtained under ^{1}H and ^{2}H decoupling conditions.

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