all lipid protons. This is presumed to result from a change in lipid dynamics and not a chemical exchange of $Ph_4B^-$. EPR experiments reveal an increase in the order parameter of both headgroup and chain-labeled lipids with high concentrations of $Ph_4B^-$,[28] and higher concentrations of $Ph_4B^-$ can fuse neutral EPC bilayers. While the time scale examined by EPR is much shorter than that for NMR, a decrease in the amplitudes of motion with $Ph_4B^-$ is consistent with previous observations and the enhanced rate of spin-diffusion seen here.

The $Ph_4B^-$ data presented here clearly indicate that intermolecular exchange is possible in membrane systems and that exchange measured with 2D spectroscopy can provide information on binding. Not all "ligands" added to membrane systems cross-relax with lipid protons; halothane, a general anesthetic, reveals no anesthetic–lipid cross-peaks even at high concentrations (data not presented). The difference between this compound and $Ph_4B^-$ presumably lies in the strength and specificity of the $Ph_4B^-$ binding.

## Conclusions

Two-dimensional cross-relaxation $^1H$ NMR can be utilized to reveal cross-relaxation pathways in phospholipid vesicle systems. Cross-relaxation among lipid protons in fluid-phase vesicles (such as sonicated egg yolk lecitin) develops over modestly long time periods (hundreds of milliseconds) and is apparently restricted to a few relaxation networks. As a result, spin-diffusion which does occur in this system does not totally obscure the useful structural information which can be obtained from the rates of magnetization exchange. Strong, rapidly developing cross-relaxation provides good evidence for a close proximity of nuclei as demonstrated by the tetraphenylborate–lipid cross-peaks. Several other noteworthy features of the 2D lipid spectra have been observed. Unlike conventional proton $T_1$ measurements, the diagonal peaks on these 2D spectra evolve with rates that are not averaged by cross-relaxation processes. Thus, the diagonal relaxation rates should reflect the local molecular dynamics and ordering. Finally, in several lipid systems asymmetry between the inside and outside surfaces of small sonicated vesicles is revealed in headgroup–alkyl chain cross-relaxation. Such cross-relaxation may provide further insight into the packing of lipids in small vesicle systems.

**Acknowledgment.** This research was supported by NSF grant BNS 8302840 and a Dreyfus Foundation grant for young faculty in chemistry (both to D.S.C.). We thank Drs. Carl Trindle and Michael F. Brown for helpful discussions during the course of this work.

**Registry No.** DOPC, 10015-85-7; LOPC, 6542-05-8; DAPC, 17688-29-8; DLPC, 18285-71-7; DPPC, 2644-64-6; $Ph_4B^-$, 4358-26-3.

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# Chemical Applications of the Two-Dimensional $^2H,^{13}C$ NMR Shift Correlation Experiment

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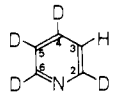
**Abstract:** Deuterium-labeling studies in mechanistic organic and bioorganic chemistry rely on the analysis of deuterated carbon sites in organic molecules. From the various techniques provided for this purpose by modern high-resolution pulse NMR spectroscopy, the two-dimensional $^2H,^{13}C$ shift correlation experiment is of particular interest. It combines the selectivity of polarization transfer with signal dispersion in two frequency dimensions. Promising analytical and mechanistic applications of this new technique are presented, and its scope is evaluated. A critical comparison of the available $^{13}C$ NMR pulse methods for deuterium-labeling studies and their relevant hardware requirements are given.

An important aspect of mechanistic studies in organic and bioorganic chemistry based on deuterated compounds is the analysis of deuterated carbon sites. In this respect, modern pulse NMR[1] provides a number of useful techniques. Simple spin-echo spectroscopy with modulation of transverse $^{13}C$ magnetization by $^{13}C,^1H$ and/or $^{13}C,^2H$ spin–spin coupling, for example, allows signals of nondeuterated carbons (C, CH, $CH_2$, $CH_3$), partially deuterated carbons (CHD, $CHD_2$, $CH_2D$), and fully deuterated carbons (CD, $CD_2$, $CD_3$) to be characterized and thus yields information about the number of protons and/or deuterons attached to a particular site.[2,3] For mixtures of deuterated and nondeuterated material, $\{^2H\}^{13}C$ polarization transfer experiments are especially helpful, because they act like a filter eliminating the resonances of nondeuterated carbons.[4,5] The spectra then only contain the signals of partially and fully deuterated groups.

In practice, due to pulse and phase imperfections in the polarization transfer experiment, the latter result is obtained only if the signal intensities of the nondeuterated positions are not dramatically different from those of the deuterated ones. For mixtures containing an excess of nondeuterated material, the signals for CH, $CH_2$, and $CH_3$ groups usually cannot be completely suppressed, which complicates, or even prevents, the interpretation of the resulting spectra. This fact is demonstrated by a polarization transfer experiment for a mixture of 55 mg of pyridine-*2,4,5,6-d*$_4$ (**1**) and 3 g of isotope-free pyridine (**2**), where the signals of the deuterated carbons can only be assigned with the help of their isotope effects (Figure 1).




**1**

We found that problems of this kind can most easily be solved with the recently described two-dimensional $^2H,^{13}C$ shift corre-

(1) For a review, see: Benn, R.; Günther, H. *Angew. Chem.* **1983**, *95*, 381; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.
(2) Wesener, J. R.; Günther, H. *Org. Magn. Reson.* **1983**, *21*, 433.
(3) Wesener, J. R.; Schmitt, P.; Günther, H. *J. Am. Chem. Soc.* **1984**, *106*, 10.
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(5) Bendall, M. R.; Pegg, D. T.; Wesener, J. R.; Günther, H. *J. Magn. Reson.* **1984**, *59*, 223.

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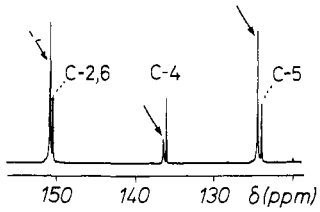



**Figure 1.** One-dimensional $\{^1H\}^{13}C$ polarization transfer experiment for a solution of 50 mg of pyridine-*2,4,5,6-d*$_4$ in 3 g of pyridine with use of the INEPT sequence[11] with continuous $^1H$ broadband decoupling (cf. Experimental Section); suppression of the CH group signals is incomplete (arrows).

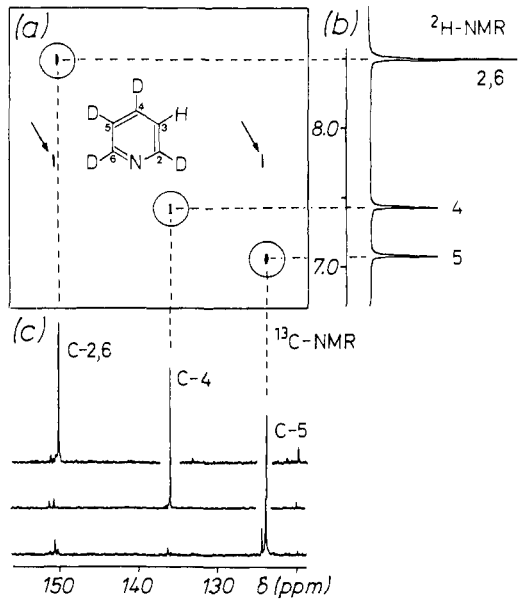



**Figure 2.** Two-dimensional $^2H,^{13}C$ shift correlation of the same pyridine solution used for the one-dimensional $\{^2H\}^{13}C$ polarization transfer experiment (Figure 1): (a) CH group signals are suppressed (C-4) or appear on the $F_1 = 0$ axis (C-2,6, C-5, arrows); (b) no corresponding $^2H$ signals are seen in the $^2H$ spectrum; and (c) $^{13}C$ cross sections of the two-dimensional data matrix.

lation experiment[6] which thus further improves the detection of deuterated carbon sites in organic compounds. In the following, we therefore describe a number of promising applications of this approach in order to demonstrate its scope, the areas where it may successfully be applied, and where it is superior to other existing NMR methods.

## Results and Discussion

In analogy to the well-known $^1H,^{13}C$ shift correlation technique, pulse sequence 1 that utilizes a $^2H$ decoupler channel in addition to $^1H$ broadband decoupling can be set up to obtain a two-dimensional shift correlation diagram between the $^2H$ and $^{13}C$ domain:

$$^2H:\ 90°(x)\text{–}t_1\text{–}\Delta_1\text{–}90°(y)\text{–}\Delta_2\text{–}^2H\text{-MLEV}$$

$$^{13}C:\ t_1/2\text{–}180°(x)\text{–}t_1/2\text{–}\Delta_1\text{–}90°(x)\text{–}\Delta_2\text{–FID} \qquad (1)$$

The evolution time $t_1$ is incremented in the usual way. The delay $\Delta_1$ determines the polarization transfer and is equal to $1/2J$, where $J$ is the appropriate one-bond $^{13}C,^2H$ coupling constant. The second delay, $\Delta_2$, is governed by the multiplicity of the $^{13}C$ signal. Optimum values are $1/4J$, $3/20J$, and $2/17J$ for CD, $CD_2$, and $CD_3$ groups, respectively.[6] $^2H$ decoupling during data acquisition is achieved by use of the MLEV technique.[7]

The advantage of such an experiment is shown in Figure 2a with the contour diagram of the two-dimensional $^2H,^{13}C$ correlated spectrum of the pyridine mixture described in the introduction. The residual signals of **2** are now suppressed (C-4) or lie on the $F_1 = 0$ axis (see arrows). No correlation is found with the $^2H$ NMR spectrum recorded independently (Figure 2b). The signals of the deuterated system **1** can easily be recognized and recorded separately from the appropriate cross sections of the two-dimensional data matrix (Figure 2c).

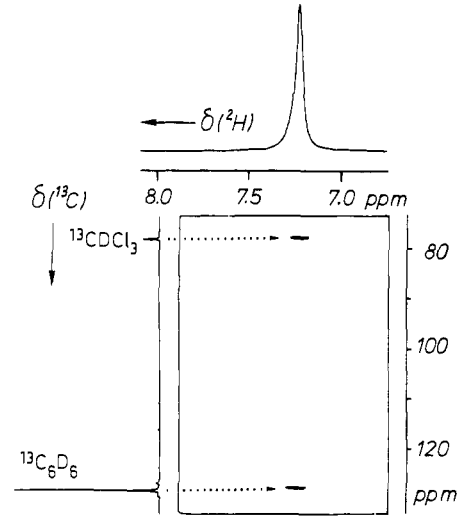



**Figure 3.** Detection of $CDCl_3$ and $C_6D_6$ in acetone/$C_6H_6$ (5:7 w/w) by $^2H,^{13}C$ shift correlation (contour plot; cf. text).

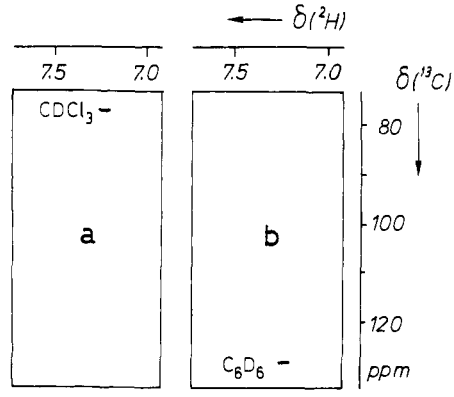



**Figure 4.** $^2H,^{13}C$ shift correlation for the detection of deuterated "impurities" (cf. text): sample a contains $CDCl_3$ and sample b $C_6D_6$.

The analytical power of $^2H,^{13}C$ shift correlation is revealed in cases where the deuterium spectrum is not resolved or cannot be assigned. Figure 3 presents a simple illustrative example which was chosen to demonstrate the principle of the new approach. It shows the superimposed $^2H$ signals of $C_6D_6$ and $CDCl_3$, dissolved in a mixture of $C_6H_6$ and acetone, as well as the result of the $^2H,^{13}C$ shift correlation that clearly distinguishes between both compounds by their different $^{13}C$ signals.[8] The additional information provided by the two-dimensional experiment is the correlation of the $^2H$ signal with a specific $^{13}C$ signal or vice versa, a fact which will be of vital importance in more complicated cases.

This aspect is further illustrated in Figure 4, where we deal with a simulated analytical problem of two samples, a and b, of a mixture of $C_6H_6$ and $CHCl_3$ that contained 0.5% (w/w) $C_6D_6$ and 2.5% (w/w) $CDCl_3$, respectively. A decision as to which sample contained the deuterated benzene and which the deuterated chloroform was not possible from either the $^2H$ or the $^{13}C$ NMR spectrum alone, since the former shows in each case a single line at the same frequency and the latter does not allow the detection of the deuterated compound in the presence of the large excess

(6) Wesener, J. R.; Schmitt, P.; Günther, H. *Org. Magn. Reson.* **1984**, *22*, 468.

(7) Levitt, M. H.; Freeman, R.; Frenkiel, T. *Adv. Magn. Reson.* **1983**, *11*, 48.

(8) In this simple case the analytical problem could also be solved by a standard one-dimensional $^1H$-decoupled $^{13}C$ NMR spectrum.

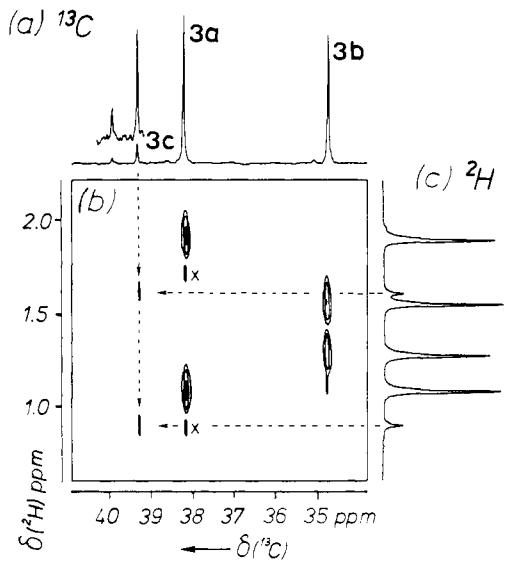
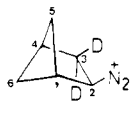



**Figure 5.** Analysis of a mixture of bicyclo[2.1.1]hexanols **3a–c** (cf. text). (a) Result of a one-dimensional $\{^2H\}^{13}C$ polarization transfer experiment using the UPT pulse sequence[12] with $^1H$ and $^2H$ decoupling; the total experimental time is 30.9 h. (b) Two-dimensional $^2H,^{13}C$ shift correlation using pulse sequence (1) with continuous $^1H$ broadband decoupling; the total experimental time is 15 h. Signals marked with (×) are $t_1$ quadrature detection artefacts and can be eliminated by more elaborate phase cycling. (c) $^2H$ spectrum (61.4 MHz) of **3a–c**.

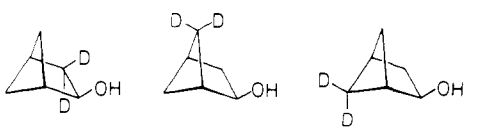
of nondeuterated material. In contrast, the shift correlation experiment clearly identifies the labeled compounds without interference from signals of nonlabeled molecules.[9]

The correlation aspect is especially important for the analysis of partially labeled compounds that arise from deuterium scrambling during the course of chemical and biochemical reactions. The $^1H$-decoupled $^2H$ spectrum very often does not allow a straightforward assignment, and the splitting pattern in the one-dimensional $^{13}C$ spectrum may not be resolved due to signal overlap.[3] Similar limitations apply to the $^1H$ spectrum. $^2H,^{13}C$ shift correlation which selects the resonances of deuterated sites and yields signal dispersion in both frequency dimensions thus is the method of choice for such investigations.

Our final example, therefore, is taken from a mechanistic study, where the fragmentation of bicyclo[2.1.1]hexyl-2-diazonium ion (**3**), dideuterated in position 3, was investigated in the presence of water.[10] The $^2H$ spectrum of the resulting alcohol mixture (Figure 5c) shows six signals and a one-dimensional $\{^2H\}^{13}C$ polarization transfer experiment yields three resonances that can immediately be assigned to deuterated carbons and an additional small signal at lowest field (Figure 5a). The shift correlation experiment (Figure 5b) clearly reveals three carbon sites as




**3**




**3a** **3b** **3c**

deuterated and shows that the $CD_2$ units stayed intact during the course of the reaction. Due to the lower sensitivity of the 2D experiment the small low-field signal found in the one-dimensional spectrum is not detected. The shift correlation also leads to a definite assignment of the $^2H$ spectrum of the product mixture, which is important for the quantitative evaluation of the reaction pathways because the $^2H$ spectrum yields the most accurate integration results. In the present case, isomers **3a**, **3b**, and **3c** were formed in 47.1, 44.9, and 8.0% yield, respectively. From the integrated $^{13}C$ spectrum (Figure 5a) we found 50.2, 43.2, and 6.6% in the same order as above.

## Conclusions

Of the various pulse methods proposed for the analysis of deuterated carbon compounds, the simple spin-echo sequences with modulation of transverse $^{13}C$ magnetisation by $^{13}C,^1H$ or $^{13}C,^2H$ coupling ($^1H$-SEFT,[3] $^2H$-SEFT[2]) are the easiest to apply. They will yield satisfactory results if signal overlap is largely absent and if the degree of deuteration is high.

A considerable improvement over these methods is achieved if the signals of nondeuterated carbons can selectively be eliminated. This is possible through the TANDEM spin-echo sequence[3] which uses simultaneous $^{13}C,^1H$ and $^{13}C,^2H$ spin-modulation, or through polarization transfer experiments based on the INEPT or DEPT sequence.[4,5]

Finally, in situations where samples with small amounts of deuterated material or compounds with a low degree of deuterium incorporation have to be analyzed, two-dimensional $^2H,^{13}C$ shift correlation, which combines the selectivity of the polarization transfer experiment with signal dispersion in two frequency dimensions, is clearly the method of choice. As other 2D techniques, however, it is less sensitive than related 1D experiments. Nevertheless, it may allow considerable time saving since integration can be limited to the $^2H$ spectrum which is unambiguously assigned by the shift correlation (cf. the experiments in Figure 5).

All of these techniques require an independent $^2H$ transmitter. In the most simple case ($^2H$-SEFT[2]), a $^2H$ decoupler serves this purpose. For $^2H,^{13}C$ polarization transfer experiments 90° $^2H$ phase shifts become essential. The relatively simple spectrometer modifications recommended by Rinaldi for this purpose,[4] however, sacrifice the possibility of simultaneous $^1H$ decoupling, which is indispensable for spectral simplification. The best solution is an external frequency synthesizer with the option of 90° phase shifts and consequently an alternative lock channel, best tuned to the $^{19}F$ frequency. A probe head tuned for $^1H$ decoupling, $^2H$ pulse excitation (observation and composite pulse decoupling), $^{13}C$ observation, and $^{19}F$ locking is thus the most versatile setup. The obvious advantages of these pulse methods over conventional investigations by $^{13}C$ or $^2H$ NMR certainly justify the cost for appropriate instrument modifications in laboratories where deuterium labeling studies are frequently performed.

## Experimental Section

Spectra were obtained with a BRUKER WH 400 NMR spectrometer equipped with pulse programmer, $^1H$ decoupler, and ASPECT 2000 data system. A probe head tuned for $^{13}C$ observation at 100.61 MHz, $^2H$ pulse excitation at 61.42 MHz, $^1H$ decoupling at 400.13 MHz, and $^{19}F$ locking at 376.5 MHz was used. The 90° pulse lengths were 24 μs ($^{13}C$) and 94.5 μs ($^2H$), respectively. $^1H$ broadband decoupling was applied throughout. $^2H$ decoupling was achieved with use of the MLEV technique[7] and the $^2H$ signal derived from a frequency synthesizer PTS 160 modified for computer-controlled 90° phase shifts. $C_6F_6$ served as internal or external lock compound. The polarization transfer experiment of Figure 1 used the INEPT sequence[4,11] with 9.62-ms delays for spin modulation and 4.81-ms delays for refocussing. For the two-dimensional shift correlation in Figure 2 the data matrix was 64 × 2048 (after zero-filling 128 × 2048). The delays $\Delta_1$ and $\Delta_2$ were equal to 19.2 and 9.62 ms, respectively, the $t_1$ increment was 7.14 ms, the relaxation delay was 4 s, and the aquisition time was 0.27 s; 256 transients were recorded. Sweep widths of ±70 Hz ($F_1$) and 3788 Hz ($F_2$) were chosen, and standard Bruker software was used for 8-step phase cycling.

For the spectra in Figures 3 and 4 the following samples were used (% w/w): Figure 3, acetone (19.7), $CDCl_3$ (47.2), $C_6D_6$ (5.5), $C_6H_6$

(9) It might be argued, that in the present case solvent effects could have been used to remove the isochrony of the $^2H$ signals of $C_6D_6$ and $CDCl_3$. While this is true, it must be emphasized that the assignment problem still remains since either one can be shifted to lower or higher field. It is only the correlation with the corresponding $^{13}C$ signal that yields the assignment.

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(27.6); Figure 4, acetone/chloroform/benzene 19.7:47.2:33.1 with 4.5% $CDCl_3$ in sample a and 1.2% $C_6D_6$ in sample b (relative to the total weight 2.5 and 0.5%, respectively). A 16 × 2048 data matrix was recorded and zero-filled to 64 × 4096 prior to transformation. Time intervals were $\Delta_1$ = 17.85 ms, $\Delta_2$ = 8.92 ms, the relaxation delay was 2 s, acquisition time was 0.17 s, and 512, 1280, and 1024 transients, respectively, were collected.

The polarization transfer $^{13}C$ spectrum of Figure 5a was obtained with the UPT pulse sequence[12] with $\theta = \pi/6 = 31.5$ μs and $\tau = 1/2J(^{13}C,^{2}H) = 25$ ms; a 10 s relaxation delay was chosen to achieve more accurate integration results. The total experimental time was 30.9 h. For the two-dimensional shift correlation (Figure 5b) a sample of 100 mg of the alcohol mixture **3a-c** in $C_6F_6$, which also served for the $^{19}F$ lock, was used (concentration 0.4 M). Sweep widths were 100 Hz ($F_1$) and 724.6 Hz ($F_2$), respectively, with quadrature detection in both dimensions and $^{1}H$ and/or $^{2}H$ decoupling as above. The $t_2$ acquisition time was 0.353 s, the relaxation delay was 2.647 s, and the number of transients in $t_2$ was 1000. The original 16 × 512 data matrix was zero-filled to 64 × 1024; a Gauss-type filter function matched for sensitivity enhancement was used in $t_2$ and a sine bell function in $t_1$. The total experimental time was 15 h.

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**Acknowledgment.** We are indebted to Dipl.-Chem. K. Finneiser, Siegen, for a sample of pyridine-*2,4,5,6-d*$_4$ and to Prof. Dr. W. Kirmse, Bochum, for a sample of the alcohol mixture **3a-c**. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

**Registry No. 1**, 94800-96-1; **3**, 94800-97-2; **3a**, 94800-98-3; **3b**, 94800-99-4; **3c**, 94842-49-6; $CDCl_3$, 865-49-6; $C_6D_6$, 1076-43-3; $D_2$, 7782-39-0; $^{13}C$, 14762-74-4.

# Acid Sites in Zeolite Y: A Solid-State NMR and Infrared Study Using Trimethylphosphine as a Probe Molecule

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*Received August 16, 1984*

**Abstract:** $^{31}P$ MAS-NMR spectra of trimethylphosphine adsorbed on H-Y zeolites have been obtained from samples calcined at 400-700 °C. For a 400 °C calcined sample, the spectrum was dominated by a resonance at ca. −3 ppm which is assigned to $[(CH_3)_3P-H]^+$ complexes that arise from chemisorption at Brønsted acid sites in the zeolite; an infrared band at 2485 $cm^{-1}$ is also attributed to this species. When this sample was degassed at 80 °C for 0.5 h, intense dipolar-derived spinning sidebands and a $J$ coupling of ~550 Hz characterized the spectrum. By contrast, the spectrum of a sample degassed for 1 h at 300 °C showed a well-resolved $J$ coupling but very weak sidebands. These results suggest the presence of at least two $[(CH_3)_3P-H]^+$ species: an immobilized complex, attributed to coordination with hydroxyl protons, and a complex which shows a high degree of motion on the NMR time scale. This latter species is stable to desorption at 300 °C. $^{31}P$ MAS-NMR spectra from samples calcined at 500 °C and above showed additional resonances in the region from ca. −32 to −58 ppm when trimethylphosphine was chemisorbed. Comparison of these shifts with model systems suggests that they arise from chemisorption to Lewis sites. The −58 ppm resonance can be ascribed to the presence of $Al_2O_3$ clusters in the zeolite at high calcination temperatures, in support of previous studies. The 500 °C calcined sample showed a resonance at −10 ppm that exhibited weak proton coupling; this resonance is attributed to a site where trimethylphosphine is coordinated to both a Lewis and a Brønsted acid site. The present study introduces trimethylphosphine as a sensitive NMR probe molecule for acidity measurements on catalytic surfaces.

The acid form of zeolites is important in a variety of catalytic reactions including hydrocarbon cracking, isomerization, and alkylation. In order to characterize these materials, one would like to know the strength and distribution of acid sites, as well as the origin of particularly strong acidity. To determine acidity, various methods have been employed such as titrating to a particular end point[1] or measuring the heat of adsorption of ammonia.[2] The infrared spectra of probe molecules such as pyridine and other bases have been used to provide evidence for both Brønsted and Lewis acid sites,[3] but distinctions within these rather broad classifications cannot generally be made.

More recently, $^{15}N$ NMR has been used to characterize acid sites on zeolites and other aluminosilicates.[4-7] Haw et al.,[7] for example, have shown that the chemical shift of $^{15}N$ in pyridine may be used to distinguish between Brønsted and Lewis sites. Moreover, *n*-butylamine is a stronger base which displaces pyridine from Brønsted sites and, at higher coverages, from Lewis sites. Estimates of the amount of Brønsted acidity can be obtained from the equivalents of *n*-butylamine required to completely displace pyridine from the Brønsted acid sites.

We have reported that trimethylphosphine reacts with protons in H-Y zeolite to form a $[(CH_3)_3P-H]^+$ complex.[8] The $^{31}P$ cross-polarized magic-angle spinning NMR (CP/MAS-NMR) spectrum of this species is characterized by a chemical shift of −2 ppm. In the absence of proton decoupling the spectrum consists of a doublet ($J \cong 550$ Hz) centered at −2 ppm, with intense, dipolar-derived spinning sidebands that are also split into doublets. Evidence for the formation of trimethylphosphonium ions in H-Y zeolite also comes from the infrared study of Schoonheydt et al.[9]

†Texas A&M University.
‡Shell Development Co.

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