solutions observed a nonlinear rate increase from 0.66 to 0.98 s^{-1} with dilution over this concentration range at 102 °C,[9] in qualitative agreement with gas-phase results.

The present study demonstrates that exchange does occur in gaseous DMF. Our kinetic parameters are consistent with an extrapolated exchange rate of 5×10^{-2} s^{-1} at 25 °C, indicating that the single ^1H methyl resonance observed in the gas phase at this temperature is not due to rapid exchange averaging. Molecular rotation in liquid *N,N*-dimethylformamide has been studied by measuring T_1 relaxation times for ^{14}N, ^{17}O, and formyl ^2H nuclei. Motion is slowest along a diffusion axis parallel to the formyl C–H bond indicating considerable anisotropic solvent interactions, which may produce the magnetic inequivalence of the CH_3 chemical shifts observed in solution.[12]

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Registry No. *N,N*-Dimethylformamide, 68-12-2.

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^{31}P Solid-State NMR of a Chemisorbed Phosphonium Ion in H–Y Zeolite: Observation of ^1H–^{31}P *J* Coupling in the Solid State

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The role of Brøsted and Lewis acidity in governing catalytic activity in zeolites and on catalytic surfaces has been extensively investigated and documented.[1] Progress has been made in acid-site determination, but there remains a need for a better method to evaluate the type, the strength, and the number of acid sites in a catalyst. Limited work on acid-site characterization using NMR has been mostly directed to ^1H NMR measurement of proton number, mobility, and position in zeolites.[2] However, more recently, advances have been made in the development of techniques and instrumentation for ***high-resolution*** studies of nuclei such as ^{13}C and ^{15}N that are of importance as possible probes of interactions between acidic sites and chemisorbed molecules on solid surfaces. Indeed, several studies using ^{13}C and ^{15}N MAS-NMR have been reported in the literature.[3] The ^{31}P nucleus is also an attractive candidate for surface characterization studies since it possesses a large chemical-shift range and is much more easily detected by NMR compared to ^{13}C and ^{15}N.

We report here ^{31}P MAS-NMR spectra from $(CH_3)_3P$ chemisorbed on a dehydrated H–Y zeolite. Evidence is presented for the presence of a chemisorbed trimethylphosphonium complex, arising from chemisorption on zeolite Brønsted sites, and physisorbed trimethylphosphine. Of special note is the observation of a heteronuclear ^1H–^{31}P *J* coupling in the solid state.

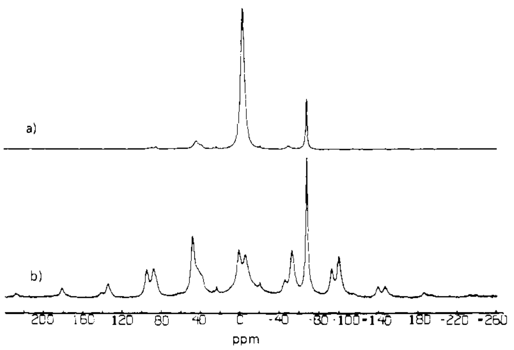

Figure 1. (a) High-power, proton-decoupled, ^{31}P MAS-NMR spectrum of trimethylphosphine adsorbed on H–Y zeolite. (b) Proton-coupled, ^{31}P MAS-NMR spectrum of the same sample. Pulse excitation, 90°, with magic-angle spinning was employed; recycle delay = 2.0 s; number of scans = 500 (Negative shifts are upfield).

A 0.5-g sample of NH_4Y zeolite was heated at 400 °C for 2 h under vacuum. The zeolite now in the HY form, was cooled to 180 °C and ~15 torr of $(CH_3)_3P$ added. Following 3-h equilibration at room temperature, the sample was finally degassed at 80 °C for 0.5 h, and then the ampule was flame sealed.[4]

As anticipated, the ^{31}P spectra were easily acquired with only ~15 min of signal averaging. Further, the phosphorus T_1's appeared to be relatively short so that direct 90° pulse excitation could be used. Thus, spectra can be acquired under conditions appropriate for direct quantification of the adsorbed species. Cross-polarization spectra were also successfully acquired, displaying the same resonances detected with 90° pulses.

Figure 1a shows the proton-decoupled, ^{31}P MAS spectrum of the solid H–Y zeolite/$(CH_3)_3P$ complex. Two distinct resonances with weak sidebands are observed at −67 and −2 ppm (relative to 85% H_3PO_4). Figure 1b shows the ^{31}P MAS-NMR spectrum taken *without* proton decoupling. The spectrum consists of a doublet ($J \simeq 550$ Hz) centered at −2 ppm, with intense spinning sidebands, and the sharp resonance at −67 ppm. Integration of the resolved peaks indicates that ~80% of the −67 ppm peak and ~60% of the −2 ppm peak (including spinning sidebands) are preserved in the proton-coupled spectrum; the "lost" intensity is presumed to be associated with severely broadened, and hence unresolved, peaks. From the individual integrated sideband intensities for the −2 ppm peaks in Figure 1b, $(M_2)^{1/2}$, the square root of the second moment, was estimated to be $\simeq$6.3 kHz.

The ^{31}P chemical shift of neat $(CH_3)_3P$ occurs at −62 ppm. Therefore, we tentatively associate the −67 ppm peak with physisorbed $(CH_3)_3P$; the observation that this peak is a singlet in the proton-coupled spectrum is also consistent with this assignment.

The −2 ppm peak is assigned to the $[(CH_3)_3P–H]^+$ chemisorbed complex on the basis of (1) the very close similarity to the chemical shift of −2.8 ppm for $[(CH_3)_3P–H]^+$ in solution[5] and (2) the observed ^1H-coupled doublet with $J \simeq 550$ Hz. The observed coupling for the $[(CH_3)_3P–H]^+$ complex in solution is ~515 Hz,[6] a value in good agreement with our observations considering the expected small changes in *J* due to differences between the solution and the solid state. The present ^{31}P NMR evidence for the formation of the $[(CH_3)_3P–H]^+$ complex is in agreement with the work of Schoonheydt et al.[7] who studied the adsorption of $(CH_3)_3P$ on H–Y zeolite and concluded that the $[(CH_3)_3P–H]^+$ complex is formed and arises from the reaction of $(CH_3)_3P$ with acidic OH groups (Brønsted sites) in the zeolite. Since cross-polarization

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(2) See, for example: Freude, D.; Pfeifer, H.; Ploss, W.; Staudte, B. *J. Mol. Catal.* **1981**, *12*, 1.

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(4) The ^{31}P MAS-NMR spectra were acquired on a Bruker CXP-200 spectrometer using a Chemagnetics probe. Cross polarization and 90° pulse methods were used in conjunction with magic-angle spinning and high-power proton decoupling. A spinning rate of 3.7 kHz was employed using nitrogen as the drive gas. The sample was transferred to the spinner while in a glovebox to minimize air contact.

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spectra were also successfully acquired, one must conclude that significant ^{1}H–^{31}P direct dipolar coupling exists for the −2 and −67 ppm species. This implies that any molecular rotational motion be either anisotropic or isotropic and in the slow correlation time limit if substantial translational diffusion is present. Since two well-resolved resonances are observed, any chemical exchange between these two sites is in the slow exchange limit.

A key feature in the NMR evidence for the $[(CH_3)_3P–H]^+$ complex is the observation of ^{1}H–^{31}P J coupling. Figure 1b represents one of the few reported heteronuclear proton J couplings observed in a solid. The only previous observation of ^{1}H J coupling in a solid is the ^{1}H–^{13}C coupling for pivalic acid,[8] a plastic crystal where molecular motional averaging is sufficient to give rise to a J-resolved spectrum, and for adamantane[9,10] and hexamethylbenzene[10] where multiple-pulse decoupling was used to remove the already motionally reduced ^{1}H–^{1}H homonuclear coupling. However, for the general case, ^{1}H-coupled, J-resolved solid-state spectra are *not* observed because (1) *direct* dipolar coupling between the ^{1}H spins and the observed nucleus is usually much larger than the *indirect* (J) coupling and (*2*) the *homo*nuclear direct dipolar coupling between protons is typically very large (>10kHz for most organic solids), rendering the overall spin Hamiltonian homogeneous. As a consequence of this latter condition, one must magic-angle spin at (unattainable) rates greater than the frequency width of the ^{1}H–^{1}H homonuclear coupling in order to eradicate the ^{1}H–^{31}P direct dipolar coupling and to obtain a high-resolution ^{31}P spectrum.[11] In the absence of a large ^{1}H–^{1}H homonuclear coupling, the ^{1}H–^{31}P direct dipolar interaction is inhomogeneous and removable by slow magic-angle spinning ($\nu_r < (M_2)_{H-P}{}^{1/2}$).

For the $[(CH_3)_3P–H]^+$ complex, the ^{1}H–^{31}P direct dipolar coupling may be estimated from a second moment calculation, yielding $(M_2)_{H-P}{}^{1/2} \sim 7.7$ kHz. This result is somewhat larger than the experimental result,[12] $(M_2)^{1/2} \sim 6.3$ kHz, but in either case shows that the *direct* dipolar coupling interaction is much larger than the measured isotropic J coupling, ~550 Hz. The estimated ^{1}H–^{1}H homonuclear contribution to the dipolar Hamiltonian is $(M_2)_{H-H}{}^{1/2} < 2.1$ kHz. This value includes both estimated contributions from methyl protons and adjacent zeolite framework protons.[13]

We conclude that the ^{31}P dipolar Hamiltonian is dominated by a reasonably large ^{31}P–^{1}H direct dipolar interaction. Thus, the ^{1}H–^{1}H coupling term serves as a minor perturbation so that the ^{31}P–^{1}H interaction is, to a good approximation, that of an isolated dipole pair, i.e., an inhomogeneous interaction. Maricq and Waugh[11] have shown from theoeretical arguments that such an interaction can be removed by slow magic-angle spinning. The anticipated result of such slow spinning ($\nu_r < (M_2)_{P-H}{}^{1/2}$) is the generation of intense dipolar-derived spinning sidebands and a J-resolved ^{31}P spectrum. This is clearly observed in the experimental spectrum (Figure 1b).[14]

Additional work is needed to develop an understanding of the factors influencing ^{31}P chemical shifts in acidic catalysts, but preliminary experiments show the ^{31}P chemical shift to appear in a distinctly different position as a consequence of interaction of the trimethylphosphine with Lewis sites.

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[14] The variation in the intensity of each doublet component in the individual sidebands may be explained[15] as arising from magic-angle spinning modulation of three anisotropic interactions, viz., the direct dipolar, the indirect dipolar,[16] and the chemical shift. This asymmetry has been discussed for the case of static samples by VanderHart and Gutowsky.[17]

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Total Synthesis of Vineomycin B_2 Aglycon

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The vineomycin A_1, A_2, B_1, and B_2 antibiotics, obtained from *Streptomyces matensis vineus*, have demonstrated activity against Gram-positive bacteria and against sarcoma 180 solid tumors in mice.[1-4] Methanolysis of vineomycin B_2 (**1**) produces compound **3**,[1] the methyl ester of vineomycin B_2 "aglycon" **2**. A notable feature of these antibiotics is the presence of a β-C-glycosidic bond joining an unsymmetrical anthraquinone to a 2,6-dideoxyglucose segment. The biological activities of the C-glycosidal vineomycins are similar, at least qualitatively, to those of the clinically important O-glycosidal adriamycin series.[5]

A total synthesis of vineomycin B_2 aglycon **3** is described herein. Two all-carbon Diels–Alder reactions using siloxy dienes[6] led to keto aldehyde **7**. A Lewis acid catalyzed hetero Diels–Alder reaction provided the C-glycoside. A Reformatsky equivalent process, using a chiral auxiliary in **9**, facilitated access to enantiomerically homogeneous aglycon **3**. The absence of a solution to the nettlesome problem of relating the remotely disposed dissymmetries of the tertiary alcohol and glycosidic segments necessitated recourse to HPLC to obtain diastereomerically homogeneous product.

Cycloaddition of the mixed ketene acetal **10**[7,8] and quinone **4**[9] followed by methylation afforded a 70% yield of **11**,[10,11,12a,b] mp 96.5–97 °C, whose conversion to the styrene-like system **12**,[12a,b] mp 139–140 °C, was smoothly accomplished (93%) through the action of $PdCl_2$–bis(acetonitrile)[13,14] in refluxing CH_2Cl_2 for 12 h. Cycloaddition of compound **12** and siloxy diene **13**[15] followed by methylation as shown gave rise to anthrquinone **14**,[12a,b] mp

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