tron-transfer scheme deduced solely from the observation of ketyls arising from the reactions of aryl ketones with reagents that can serve as hydride donors and bases.

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Gas-Phase ^{13}C NMR Spectra and Exchange Kinetics of *N,N*-Dimethylformamide

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Recently, gas-phase NMR kinetic studies of *N,N*-dialkyl-substituted formamides have appeared.[1-3] The simplest molecule of this type, *N,N*-dimethylformamide, presents special problems due to the temperature-independent magnetic equivalence of the ^{1}H dimethylamino resonances in the gas phase.

The present study reports gas-phase ^{13}C NMR spectra of *N,N*-dimethyl-$^{13}C_2$-formamide (DMF), consistent with first-order exchange rates attributable to the internal rotation process, which are ca. 6.7 times faster than corresponding solution values. The gas-phase value of the free activation energy, $\Delta G^{\ddagger}$ is 19.4 (0.1) kcal/mol, approximately 1.5 kcal/mol lower than values obtained for the neat liquid and solutions in CCl_4, and is consistent with a process having a transition state with greater steric requirements than the molecule's equlibrium configuration.[1,2]

We recently obtained ^{1}H spectra of DMF at 500 MHz at 23 °C for a sample containing 1100 torr of SF_6 and DMF at its vapor pressure (ca. 0.8 torr) which showed a single resonance (2.88 ppm relative to gaseous Me_4Si, 5.7-Hz fwhm) for the dimethylamino proton resonances. The line widths of the formyl proton resonance was 5.8 Hz. Previous attempts to resolve the ^{1}H dimethylamino resonances of gaseous DMF at 100 and 360 MHz were also unsuccessful.[3,4] In contrast, in a 10% solution in CCl_4, at 500 MHz the dimethylamino resonances are separated by 83.15 Hz. In order to determine if the suprising magnetic equivalence of the dimethylamino proton resonances in the gas phase is due to rapid exchange or structural factors, we investigated the gas-phase ^{13}C spectrum of DMF.

A sample containing 25 μL of 99% ^{13}C-enriched DMF (MSD isotopes) and 1000 torr of SF_6 in a 6 cm long, 20 mm o.d. tube was used to obtain rate data. The high SF_6 partial pressure ensured first-order rates. On the basis of RRKM calculations and previous gas-phase studies of amides,[1,3] the transition to second-order kinetics for this system is expected at pressures below ca. 10 torr. All ^{13}C NMR measurements were made with a Nicolet 4.8T spectrometer with ^{13}C observation at 50.307917 MHz. Proton-decoupled gas-phase spectra were acquired in an unlocked mode. Decoupler powers of 2.5 W were supplied to the sample between and 8.5 W during the acquisition pulse, respectively. Typically 2000 free induction decays were acquired and stored in 2 K to produce frequency domain spectra with signal/noise ratios of ca. 50/1. Acquisition times were typically 256.25 ms/transient with a 2.75-s delay and a 90° pulse angle (50 μs). At 50° T_1 values for the up- and downfield ^{13}C resonances are 0.29 (8) and 0.25 (3) s, respectively.[5] Temperatures were controlled with a 0.1 °C pyrometer. The temperature was calibrated at 10-deg intervals with a copper–constantan thermocouple placed in a nonspinning tube, under the same experimental conditions, i.e., decoupling power and repetition rate, used to obtain rate data.

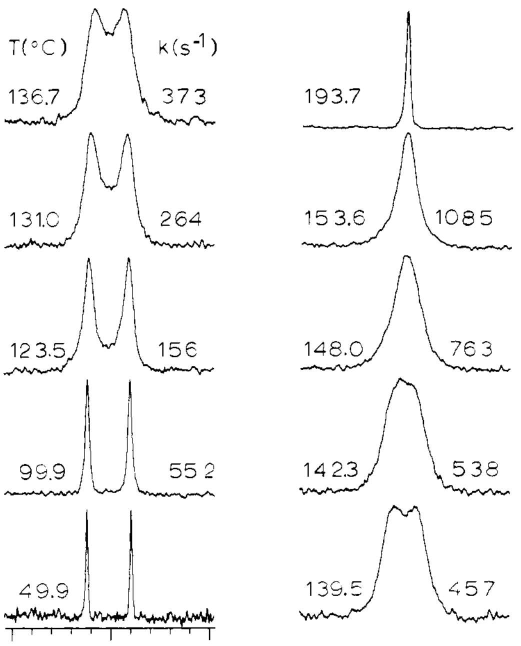

Figure 1. Gas-phase ^{13}C NMR spectra of *N,N*-dimethyl-$^{13}C_2$-formamide. Spectral acquisition parameters are described in the text.

Rates were calculated with the computer program DNMR5,[6] which uses a nonlinear least-squares regression analysis to obtain the best fit of the experimental spectrum. All free induction decays were multiplied by an exponential line-broadening factor of 8.0 Hz, after zero filling to 4K. The digital resolution was 1.95 Hz/point. Typically 900 experimental points were used in the analysis of each spectrum. The effective line-width parameter, T_2, was measured at 30 °C and between 180 and 200 °C and was estimated assuming a linear temperature dependence at each temperature where experimental rate data were obtained. A limiting chemical shift difference of 228.0 ± 2 Hz was obtained at 30.0 °C. Within our experimental uncertainty limits, limiting ^{13}C chemical shifts for gaseous DMF are not temperature dependent. Each spectra was analyzed as an AX system with a $^{3}J_{^{13}C-^{13}C}$ coupling constant of 1.92 Hz, which was measured for a liquid sample containing ca. 1% DMF in D_2O.

Figure 1 displays temperature-dependent gas-phase ^{13}C spectra of DMF and associated rate constants obtained from the analysis described above. The coalescence temperature for the ^{13}C resonances occurred at 142.3 °C. Analysis of the temperature dependence of 15 rates obtained between 109.3 and 156.4 °C yielded the following kinetic parameters: $E_{act}(\infty)$, 20.5 (0.3) kcal/mol; $\Delta H^{\ddagger}$, 19.7 (0.3) kcal/mol; $\Delta S^{\ddagger}$, 1.0 (0.8) cal/(mol K); $\Delta G^{\ddagger}_{298}$, 19.4 (1) kcal/mol. The small entropy value observed in this experiment is consistent with previous results obtained for similar molecules in the gas phase.[1,2] Previous ^{13}C liquid kinetic studies that employed line-shape analysis and application of the Forsen–Hoffman spin-saturation method reported a $\Delta H^{\ddagger}$ of 20.39 kcal/mol,[7,8] in good agreement with a ^{1}H line-shape analysis[9] and variable field coalescence measurements.[10] Faster gas-phase exchange rates and lower gas-phase $\Delta G^{\ddagger}$ values are consistent with a process proceeding via a transition state with greater steric requirements than the equlibrium conformation.[1,2] Dilution studies that varied the mole fraction of DMF from 1 to 0.167 in CCl_4

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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 ^{1}H 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 ^{2}H 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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^{31}P Solid-State NMR of a Chemisorbed Phosphonium Ion in H–Y Zeolite: Observation of ^{1}H–^{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 ^{1}H 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 ^{1}H–^{31}P *J* coupling in the solid state.

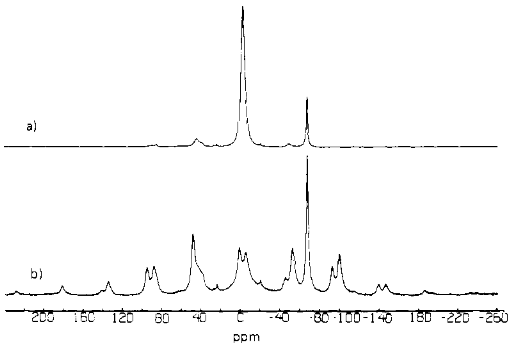

Figure 1. (a) High-power, proton-decoupled, ^{31}P MAS-NMR spectrum of trimethylphosphine adsorbed on H–Y zeolite. (b) Proton-coupled, ^{31}P MAS-NMR spectrum of the same sample. Pulse excitation, 90°, with magic-angle spinning was employed; recycle delay = 2.0 s; number of scans = 500 (Negative shifts 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 $\sim$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 $\sim$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 $\sim$80% of the −67 ppm peak and $\sim$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 $[(CH_3)_3P\text{–}H]^+$ chemisorbed complex on the basis of (1) the very close similarity to the chemical shift of −2.8 ppm for $[(CH_3)_3P\text{–}H]^+$ in solution[5] and (2) the observed ^{1}H-coupled doublet with $J \simeq 550$ Hz. The observed coupling for the $[(CH_3)_3P\text{–}H]^+$ complex in solution is $\sim$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 $[(CH_3)_3P\text{–}H]^+$ 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 $[(CH_3)_3P\text{–}H]^+$ 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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