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Determination of the Internal Rotation Barrier of [^{15}N]Formamide from Gas-Phase ^{1}H NMR Spectra

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We report gas-phase exchange-broadened ^{1}H NMR line shapes of formamide (FA) which are temperature and pressure dependent. Rate constants for internal rotation of the amide group of unsolvated FA, obtained between 318.3 and 333.1 K for a sample containing FA at its vapor pressure (1−3 Torr), 3452.3 Torr of SF_6 and 68.1 Torr of TMS, are consistent with a high pressure limit activation energy, $E_\infty = 16.6(0.3)$ kcal mol^{-1}, and an Arrhenius *A*-factor, $A_\infty = 1.60(1.02) \times 10^{13}$ s^{-1}.[1]

The gas-phase E_∞ is close to recent theoretical estimates.[2,3−12] Barriers to internal rotation of the amide group of FA, calculated within the last 10 years, range from 14.2 to 18.7 kcal mol^{-1} with the more recent results converging in the 15−16 kcal mol^{-1} range.[3−12] The most recent calculation,[3] at the CCSD(T) electron correlation level using a PVTZ basis set, yielded a 15.8 kcal mol^{-1} barrier, excluding zero point energy (ZPE) corrections. Including ZPE corrections the barrier is estimated as 15.2(0.5) kcal mol^{-1} where the uncertainty arises from the basis set dependence of calculated vibrational frequencies.[3] Prior to this report, only experimental data for solvated FA were available for comparison.[13−15] Experimentally determined E_{act} values obtained for FA solutions from NMR measurements range from 16.8(1.0) kcal mol^{-1} (dioxane solution)[13] to 21.3(1.3) kcal mol^{-1} (water solution).[14] E_{act} for neat liquid FA is 18.9(1.0) kcal mol^{-1}.[15] Theoretical studies indicate that solvation significantly increases the internal rotation barrier of FA.[16,17] A recent theoretical study using the effective fragment method calculated a barrier increase of 3.7 kcal mol^{-1} with solvation of FA in water.[16] The reported E_{act} for FA in water is 4.7(1.4) kcal mol^{-1} higher than the gas-phase E_∞, in agreement with this prediction.

Obtaining the experimental gas-phase barrier to internal rotation of the amide group of FA has proven to be very difficult. The height of the barrier and the fact that internal rotation and nitrogen inversion are strongly coupled has prevented a determination of the barrier height from rotational and vibrational data.[18,19] Although gas-phase barriers to internal rotation for several larger N-alkyl-substituted amides have been determined from analysis of exchange-broadened NMR spectra,[20] previous attempts to determine the barrier to internal rotation of FA by this method were unsuccessful. FA is less volatile and has fewer equivalent protons than the larger amides which have been successfully studied. Also, the proton resonances of the ^{14}N isotopomer are broadened by quadrupolar relaxation, while those of the ^{15}N isotopomer are split into doublets, further reducing spectral intensity. Recently, the fast-exchange ^{1}H chemical shifts and average $^1J_{\mathrm{NH}}$ and $^2J_{\mathrm{NH}}$ coupling constants of FA in the gas phase at ca. 483 K were reported.[21] Slow exchange and exchange-broadened gas-phase spectra of FA have not been observed previously.

Gas-phase NMR spectra of FA were obtained using a wide-bore NT-300 spectrometer controlled by a Tecmag Taurus data system with proton observation at 300.07 MHz equipped with a 12 mm ^{1}H Bradley probe. Measurements were made on spinning samples using a 90° flip angle (14 μs pulse) with a 1 s delay. The estimated spectrometer field drift was 0.05 Hz/h and frequency locking was not employed. Typically, 30 000 free induction decays were acquired and stored in 8K to produce frequency domain spectra of sufficient quality for fitting. Temperature control and measurement have been described previously.[22] Samples equilibrated for at least 10 min prior to data acquisition. To minimize wall adsorption and maximize signal-to-noise at low temperatures, slow exchange spectra of FA were obtained in Teflon sample cells. These sample tubes were constructed of 3-cm-long sections of thin Teflon tubing fitted at each end with Teflon plugs. These tubes were then inserted into longer 12-mm-o.d. Wilmad high-precision tubes for introduction into the probe. The samples were prepared by placing a small drop of liquid FA (Isotec Inc., 99% purity) in the bottom of a tube with TMS added as a frequency and resolution reference. Samples containing various amounts of SF_6, which has a high collision efficiency for activating conformational processes,[24] were used to determine the pressure required to reach the unimolecular region. They were prepared in restricted volume NMR tubes constructed from 3-cm-long sections of Wilmad high-precision 12-mm coaxial inserts. Nine samples were prepared by deposition of a small drop of FA in the bottom of the sample tube, adding at least 60−70 Torr of TMS and between 1100 and 4500 Torr of SF_6. Cooled sample tubes were quickly torch sealed and immersed in liquid nitrogen. Samples with total pressures above 3800 Torr were similarly prepared in 12-mm-o.d. heavy-walled Wilmad NMR tubes.

The slow exchange spectrum of gaseous ^{15}N FA, an ABCX spin system, obtained at 302.1 K consists of three broad resonances at 4.71, 4.49, and 4.21 ppm (amino protons) and a broad multiplet at 8.12 ppm (formyl proton) downfield from gaseous TMS. The three broad resonances near 4.5 ppm in the

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[1] We report these parameters because RRKM theory may not provide a valid description of the kinetics of the exchange process and interpretation of the Eyring parameters may be problematic.

[2] The critical energy, E_{o}, the difference between the ZPE of the ground state and the ZPE of the transition state, is comparable to a calculated barrier which includes ZPE corrections. Assumming ground and transition state partition functions are equal and intramolecular vibrational redistribution is ergodic, $E_{\mathrm{o}} = E_\infty - RT$. See: Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; John Wiley and Sons: New York, 1996; p 116.

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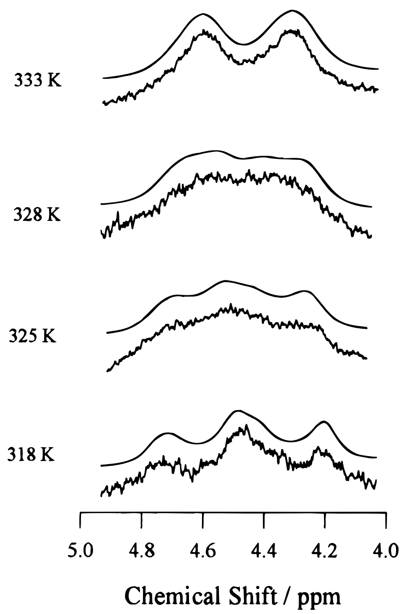

Figure 1. Temperature dependence of the N−H resonances of [^{15}N]-formamide at 300 MHz. Top and bottom traces correspond to calculated and experimental spectra. The sample contained 3452.3 Torr of SF_6, 68.1 Torr of TMS, and 1−3 Torr of [^{15}N]formamide.

undecoupled spectrum arise from two overlapping doublets with $^1J_{NH}$ ca. 85 Hz since the ^{15}N-decoupled[24] slow exchange spectrum of gaseous FA at 313.3 K only shows two resonances in this region at 4.64 and 4.39 ppm ($\Delta\nu = 75$ Hz).

Exchange-broadened line shapes obtained at 333.2 K demonstrate that rate constants are independent of pressure above 3.2 atm. ^{15}N-coupled spectra of a sample containing 1−3 Torr of ^{15}N FA, 3452.3 Torr of SF_6, and 68.1 Torr of TMS were analyzed to obtain a series of temperature-dependent rate constants. Decoupling was not used during acquisition of exchange-broadened spectra since it does not result in signal enhancement and can increase the temperature gradient in the sample cells, and the greater complexity of the undecoupled spectra allows rate constants to be determined more accurately. At fast exchange (ca. 348 K), the amino proton resonances of this sample appear as a doublet ($^1J_{NH} = 87.3$ Hz) centered at 4.53 ppm and the formyl resonance appears as two triplets with $^2J_{NH} = 20.14$ Hz and $^3J_{HH} = 6.71$ Hz. Exchange-broadened spectra were obtained at nine temperatures between 318.3 and 333.1 K. Rate constants were calculated with the computer program DNMR5[25] which uses an iterative nonlinear least-squares regression analysis to obtain the best fit of the experimental NMR spectrum. The method used for estimating the effective T_2 for each spectrum has been described previously.[22] It was not possible to obtain slow exchange coupling constants for gas-phase FA and previously reported coupling constants which are consistent with our measured fast exchange averages were used.[15,21] Typically 800 experimental points were used in the analysis of each spectrum. Each spectrum was analyzed by iterating on the rate constant, spectral origin, baseline height, and baseline tilt. All other parameters were held constant. Figure 1 shows representative experimental and calculated ^{1}H spectra of the ^{15}N-coupled amino proton resonances of FA at four temperatures. The rate constants obtained are the following: 62.8(1.9) s^{-1} at 318.3 K; 75.9(1.3) s^{-1} at 320.4 K; 86.3(1.3) s^{-1} at 321.8 K; 100.96(1.3) s^{-1} at 323.8 K; 117.6(1.9) s^{-1} at 325.7 K; 132.5(2.1) s^{-1} at 327.1 K; 160.3(0.6) s^{-1} at 330.1 K; 178.4(0.1) s^{-1} at 331.7 K; 210.8(1.1) s^{-1} at 333.1 K. Reported uncertainties are 2σ. An Arrhenius plot of these data is shown in Figure 2. Arrhenius parameters were obtained from a weighted least-squares regression with weights assigned in the customary manner.[26]

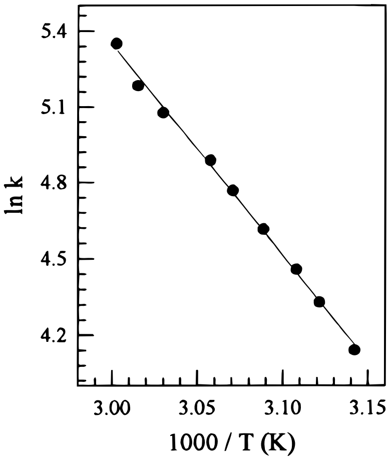

Figure 2. Arrhenius plot of gas-phase exchange rate constants of [^{15}N]-formamide for a sample containing 3452.3 Torr of SF_6, 68.1 Torr of TMS, and 1−3 Torr of [^{15}N]formamide. $E_\infty = 16.6(0.3)$ kcal mol^{-1} and $A_\infty = 1.60(1.02) \times 10^{13}$ s^{-1}.

Pressure dependent spectra will be reported in a subsequent paper.

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