Intermolecular Conversion over a Low Barrier. 3. Gas-Phase NMR Studies of an H Bond Association

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Abstract: Gas-phase NMR spectra of mixtures of $(CH_3)_2O$ and HCl were recorded for mole ratios 1:1 → 1:4, at total pressures of 400–40 torr, over the temperature range 300–212 K, in order to investigate the kinetics of formation of the $(CH_3)_2O$:HCl complex. The results gave only a lower bound for the dissociation rate constant, in the limiting low-pressure regime, and confirmed the published thermochemical values for association: $\Delta H° = -6.9$ kcal/mol and $\Delta S° = -25.6$ eu. Two of the low wagging frequencies proposed for the complex had to be raised from 50 to 100 cm^{-1} to obtain agreement between the calculated and observed $\Delta S°$. The NMR spectra provide a reliable value for the increment in the proton chemical shift due to hydrogen bond formation and enable estimates to be made of equilibrium vapor pressures of $(CH_3)_2O$:HCl at several temperatures (212 → 233 K). The kinetics of dissociation are in the second-order regime, and the activation energy for dissociation cannot be greater than 8.5 kcal/mol.

The unique features of hydrogen-bonded systems have been probed, both experimentally and theoretically, for about 6 decades. The wide variety of structures in which they occur have been examined, their spectra recorded, and in many cases the relevant thermochemistry of formation and dissociation determined. Their existence has been formulated in terms of a multitude of electronic models. Yet, because of the comparative weakness of hydrogen bonds and their consequent very high rates of dissociation, little is established relative to the dynamics of their formation/fragmentation. In view of their pervasiveness in naturally occurring systems, both in vivo and vitro, it is worthwhile to determine whether state-of-art techniques can give measures of times required for relaxation to equilibrium of perturbed hydrogen-bonded systems. Here we report on the use of gas-phase NMR spectra, from which one can estimate chemical exchange rates between free and hydrogen-bonded HCl from resonance line shapes. Ultimately we hope to answer several interesting questions: (a) At what gas density do dissociation rates of hydrogen-bonded species begin to "fall-off" toward second-order kinetics? (b) Given the measured enthalpy of dissociation for a particular type of bond, is its dissociation rate correctly predicted by conventional reaction rate theory, in view of the low density of states at $E°$ ($\approx 280/cm^{-1}$)? (c) Are there experimental measures of exchange rates for H(D) atoms between two unequal potential wells, which are typical of most hydrogen bonds, for comparison with theoretical estimates?

We succeeded in answering question a, question b in part, and question c in the negative for one of the simplest hydrogen-bonded species: $(CH_3)_2O + HCl \rightleftharpoons (CH_3)_2O$:HCl. We had hoped that

at the available sensitivities we could reach conditions in the gas phase for the NMR spectra of bound and free HCl to be resolved before becoming limited by condensation of the adduct. This model system was chosen because its thermochemistry and spectroscopy have already been extensively investigated. In particular, the enthalpy and entropy of association have been measured from the temperature variation of the equilibrium vapor pressure,[1] of its infrared spectra,[2] from NMR spectra recorded for mixtures at relatively high pressures[3] (3.3 atm ≤ p ≤ 11.6 atm), and from Raman spectra[4] (22 ≤ T °C ≤ 132). On this basis we accepted the weighted mean for $\Delta H° = -6.9$ kcal/mol and $\Delta S° = -25.6$ eu. Our computations of the partition functions needed for the thermochemical and kinetic parameters were greatly facilitated by the assigned vibrational frequencies of the dimethyl ether[5] and of the complex.[6] While the molecular dimensions of the ether are well established,[7] we were forced to postulate a structure for $(CH_3)_2O$:HCl (Figure 1) by analogy with adducts such as H_2CO:HF; H_2O:HCl, etc.[8] but unlike furan:HCl.[9] The molecular constants for HCl were taken from Herzberg's tables.[10]

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Table I. Calculated Equilibrium Concentrations (mol cm^{-3})

	T, K	K_c	$[C]_{eq}$	$[\epsilon]_{eq}$	$[HCl]_{eq}$[a]	δ_{obsd}(corr)
α	296.7	7.478 (+3)	1.991 (−7)	5.164 (−6)		−0.226
	274.2	1.806 (+4)	4.351 (−7)	4.928 (−6)		−0.125
	252.0	5.064 (+4)	9.439 (−7)	4.419 (−6)		0.105
	241.6	8.787 (+4)	1.301 (−6)	4.062 (−6)		0.352
	226.8	2.107 (+5)	1.859 (−6)	3.504 (−6)		
	211.6	5.906 (+5)	2.316 (−6)	3.047 (−6)		
β	296.7	7.479 (+3)	5.170 (−8)	2.630 (−6)		−0.277
	274.2	1.806 (+4)	1.184 (−7)	2.563 (−6)		−0.166
	252.0	5.064 (+4)	2.864 (−7)	2.395 (−6)		−0.072
	241.6	8.787 (+4)	4.295 (−7)	2.252 (−6)		0.087
	226.8	2.107 (+5)	7.114 (−7)	1.970 (−6)		0.309
	211.6	5.906 (+5)	1.019 (−6)	1.663 (−6)		
γ	299.6	6.743 (+3)	6.907 (−7)	1.014 (−5)		−0.158
	296.3	7.587 (+3)	7.650 (−7)	1.007 (−5)		−0.096
	254.4	4.489 (+4)	2.672 (−6)	8.164 (−6)		0.335
δ	211.9	5.778 (+5)	3.012 (−7)	7.823 (−7)		0.160
η	296.6	7.506 (+3)	6.840 (−8)	3.020 (−6)		−0.303
	241.4	8.885 (+4)	5.470 (−7)	2.541 (−6)		0.137
I	293	8.562 (+3)	3.084 (−7)	5.542 (−6)	6.517 (−6)	−0.233
	273	1.901 (+4)	6.117 (−7)	5.239 (−6)	6.214 (−6)	−0.107
	253	4.815 (+4)	1.194 (−6)	4.657 (−6)	5.632 (−6)	0.150
II	263	2.970 (+4)	4.863 (−7)	2.737 (−6)	6.069 (−6)	−0.143
	243	8.136 (+4)	9.574 (−7)	2.266 (−6)	5.598 (−6)	0.124
	233	1.441 (+5)	1.264 (−6)	1.960 (−6)	5.291 (−6)	0.060
III	263	2.970 (+4)	2.581 (−7)	1.367 (−6)	6.405 (−6)	−0.235
	243	8.136 (+4)	5.262 (−7)	1.099 (−6)	6.137 (−6)	−0.090
	233	1.440 (+5)	7.110 (−7)	9.142 (−7)	5.952 (−6)	−0.026
	223	2.670 (+5)	9.019 (−7)	7.233 (−7)	5.761 (−6)	−0.171

[a] In samples $\alpha \rightarrow \eta$, $[HCl]_{eq} = [\epsilon]_{eq}$.

Experimental Section

(a) Five samples were prepared at Cornell University in 15-mm (o.d.) tubes. These were first thoroughly treated with Si(CH$_3$)$_3$Cl under reflux conditions, to convert all surfaces to a "hydrophobic" state. They were then washed in hexane, pumped down, filled (at 296 K), and sealed.[11] The pressures (in torr) used (ether/acid) were α (99/99), β (49.5/49.5), γ (200/200), δ (20/20), and η (57/57). The NMR spectra were recorded by a Bruker WM300 unit at 300.133 MHz. Generally 3000–10000 scans were required. Sample spectra are shown in Figure 2.

(b) Another set of samples was prepared at the Institute for Molecular Science in 5-mm tubes which were not treated with the trimethylsilyl chloride, but they were thoroughly degassed. The pressures (ether/acid) used were I (108/126), II (59.5/121), and III (30/123). The NMR spectra were recorded by a JEOL GX400, operating at 399.97 MHz, and required 300–1200 scans for typical S/N levels as shown in Figure 3.

Inspection of these spectral scans shows that within the fluctuations inherent in the spectrometers the chemical shift for ^{1}H$_{CH_3}$ is unaffected by hydrogen bonding. These are typically intense, very narrow resonances. In contrast, the resonances of ^{1}H$_{Cl}$ are weak and relatively broad, and they are clearly shifted to lower fields when the concentration of the complex was increased, i.e., by lowering the temperatures or raising the pressures of the reagents. At the lowest pressures and temperatures for which useful spectra could be recorded there was only a single, exchange-averaged O⋯HCl line. Furthermore, the line broadened somewhat (~10%) at higher temperatures, which is opposite to that expected for broadening due to chemical exchange. It is, however, consistent with the effects of quadrupole relaxation of Cl nuclei upon the H–Cl spin–spin coupling.

When the probe temperatures were lowered, both spectrometers became somewhat unstable and the shimming conditions drifted. The resonance positions were no longer precisely reproducible. Since we are primarily interested in the *changed* location of ^{1}H$_{Cl}$ due to hydrogen bonding, and since the chemical shift of the methyl protons is negligibly affected by such bonding, we selected the latter to serve as an *internal standard*. We located the chemical shift of ^{1}H$_{Cl}$ relative to the much
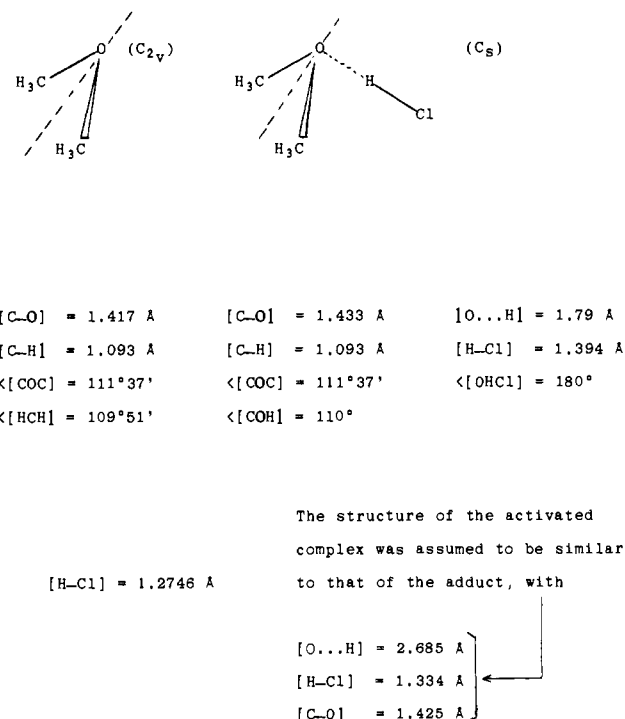
(10) G. Herzberg, "Spectra of Diatomic Molecules", D. VanNostrand Co., Inc., New Jersey, 1950.

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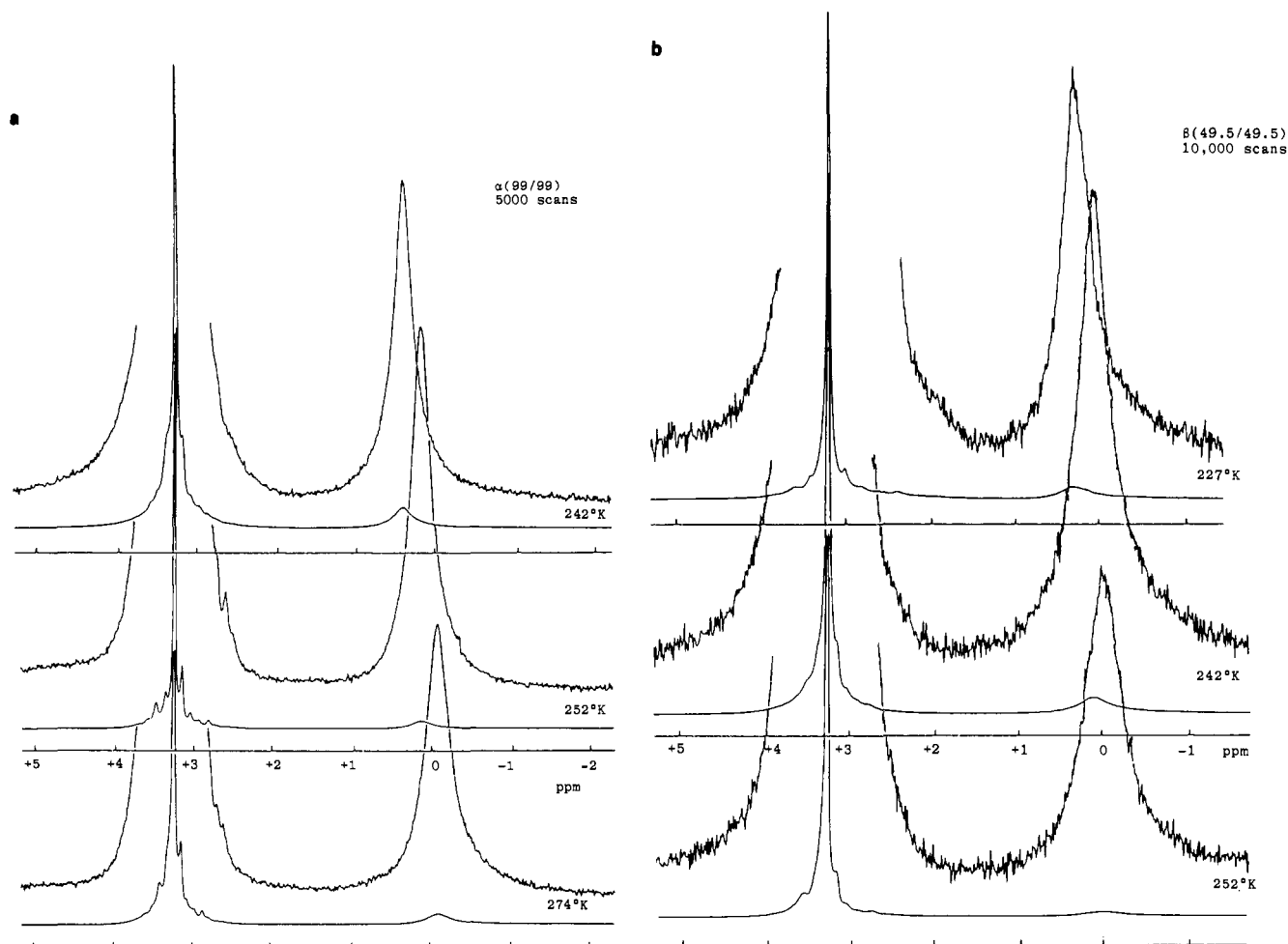
[C–O] = 1.417 Å   [C–O] = 1.433 Å |O⋯H| = 1.79 Å

[C–H] = 1.093 Å   [C–H] = 1.093 Å   [H–Cl] = 1.394 Å

<[COC] = 111°37'   <[COC] = 111°37'   <[OHCl] = 180°

<[HCH] = 109°51'   <[COH] = 110°

[H–Cl] = 1.2746 Å

The structure of the activated complex was assumed to be similar to that of the adduct, with

[O⋯H] = 2.685 Å
[H–Cl] = 1.334 Å
[C–O] = 1.425 Å

Figure 1. Relevant molecular structures.

stronger and clearly narrower methyl position; we assigned ^{1}H$_{CH_3}$ as 3.221 ppm, downfield from Me$_4$Si (0). Table I is a compilation of all the data thus recorded (δ_{obsd}, ppm).

Data Reduction

The first step necessitated calculation of the composition actually present for each of the recorded spectral scans. Since the experimental mixtures were prepared at room temperature and sealed in fixed volumes, it was convenient to express the ther-

Figure 2. NMR spectra recorded with Bruker WM300 at Cornell University, operating at 300.133 MHz. The sharp peak at 3.22 ppm is due to CH_3; the broad resonance at ≈ 0 ppm is due to H-bonded HCl.

mochemical equilibrium constant as $K_c = (2.082 \times 10^{-4})T$ exp-$(+3472.6/T)$, in units of $(mol\ cm^{-3})^{-1}$. These are also listed in Table I. For the reaction (ether + acid → complex)

$$\epsilon + A \underset{k_a}{\overset{k_d}{\rightleftharpoons}} C$$
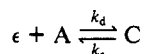
$K_c = k_a/k_d = \tau_b/\tau_f[\epsilon]$, where τ_f is the mean time which the acidic protons spend in free HCl, and τ_b is the mean time which they spend in hydrogen-bonded structures. The chemicalf shift recorded for $^1H_{Cl}$ under rapid exchange conditions is

$$\delta_{obsd} = \frac{\delta_b\tau_b + \delta_f\tau_f}{\tau_b + \tau_f} = \frac{\delta_f + \delta_bK_c[\epsilon]}{1 + K_c[\epsilon]}$$

Hence a plot of $\delta_{obsd}\{1 + K_c[\epsilon]\}$ vs. $K_c[\epsilon]$ should be linear, with an intercept equal to δ_f [i.e., the chemical shift for free HCl], and a slope which is the chemical shift for $^1H_{Cl}$ when hydrogen bonded to ether. All the points listed in the table were plotted in Figure 4. With the exception of four low-temperature points there is excellent agreement between the values derived from different preparations, with spectra recorded on two very different spectrometers, over a range of mole fractions (1:1–1:4). This validates our accepted magnitudes for $\Delta H°$ and $\Delta S°$.

The least squares line (correlation coefficient 0.992), exclusive of the four deviant points, has an intercept, $\delta_f = -0.321 \pm 0.01$ ppm, in good agreement with the directly measured value for 100 torr of HCl [−0.33 ppm on the Bruker and −0.331 ppm on JEOL]. The slope of the line gives δ_b : 2.189 ± 0.063 ppm. Hence the increment on hydrogen bond formation is 2.510 ppm.

The frequency differences between free and hydrogen-bonded $^1H_{Cl}$ are 753 and 1004 Hz on the Bruker and JEOL spectrometers, respectively. At the coalescence condition these translate to τ_{NMR}^{-1} ($\approx 2^{1/2}\pi\Delta\nu$) equal 3345 and 4461 s^{-1}. We conclude that the

chemical exchange time at the lowest pressures and temperatures used in these experiments is less than 2.99×10^{-4} s (Bruker), and more tightly *less than 2.24×10^{-4} s* (JEOL). We estimate that measurement of this rate would be possible were the sensitivity of NMR units increased by a factor of 10, i.e., so that acceptable spectra could be recorded for lower pressure samples.

Vapor Pressure of $(H_3C)_2O\cdot HCl$

The four low-temperature points at 212, 223, 227, and 233 K fall significantly below the line fixed by the other 21 points because small amounts of the complex had condensed under those conditions. These allow us to estimate the vapor pressure of the complex at the indicated temperatures, even though it exists only in the presence of its decomposition products. Note that

$$[\epsilon]_{vapor} = \frac{\delta_{obsd} - \delta_f}{(\delta_b - \delta_{obsd})K_c}$$

Since δ_b, δ_f, K_c, and δ_{obsd} are known for each of the deviant points, $[\epsilon]_{vapor}$ can be calculated. Also, mass balance requires

$$[\epsilon]_{vapor} + [C]_{vapor} + [C]_{llq} = [\epsilon]°$$

$$[A]_{vapor} = [A]° - [C]_{vapor} - [C]_{llq} = [A]° - [\epsilon]° + [\epsilon]_{vapor}$$

$$K_c = \frac{[C]_{vapor}}{[\epsilon]_{vapor}\{[A]° - [\epsilon]° + [\epsilon]_{vapor}\}}$$

Hence $[C]_{vapor}$ can be evaluated; this is the equilibrium vapor pressure of the complex. Since these four points encompass a very short temperature range, a van't Hoff plot proves misleading. However, if we accept a normal Trouton's constant for the complex [$\Delta S°$ vaporization ≈ 22 eu] we deduce at 233 K, $p \approx 11.9$ torr ($\Delta H_{vap} = 7.05$ kcal/mol); at 227 K, $p \approx 7.5$ torr ($\Delta H_{vap} = 7.07$
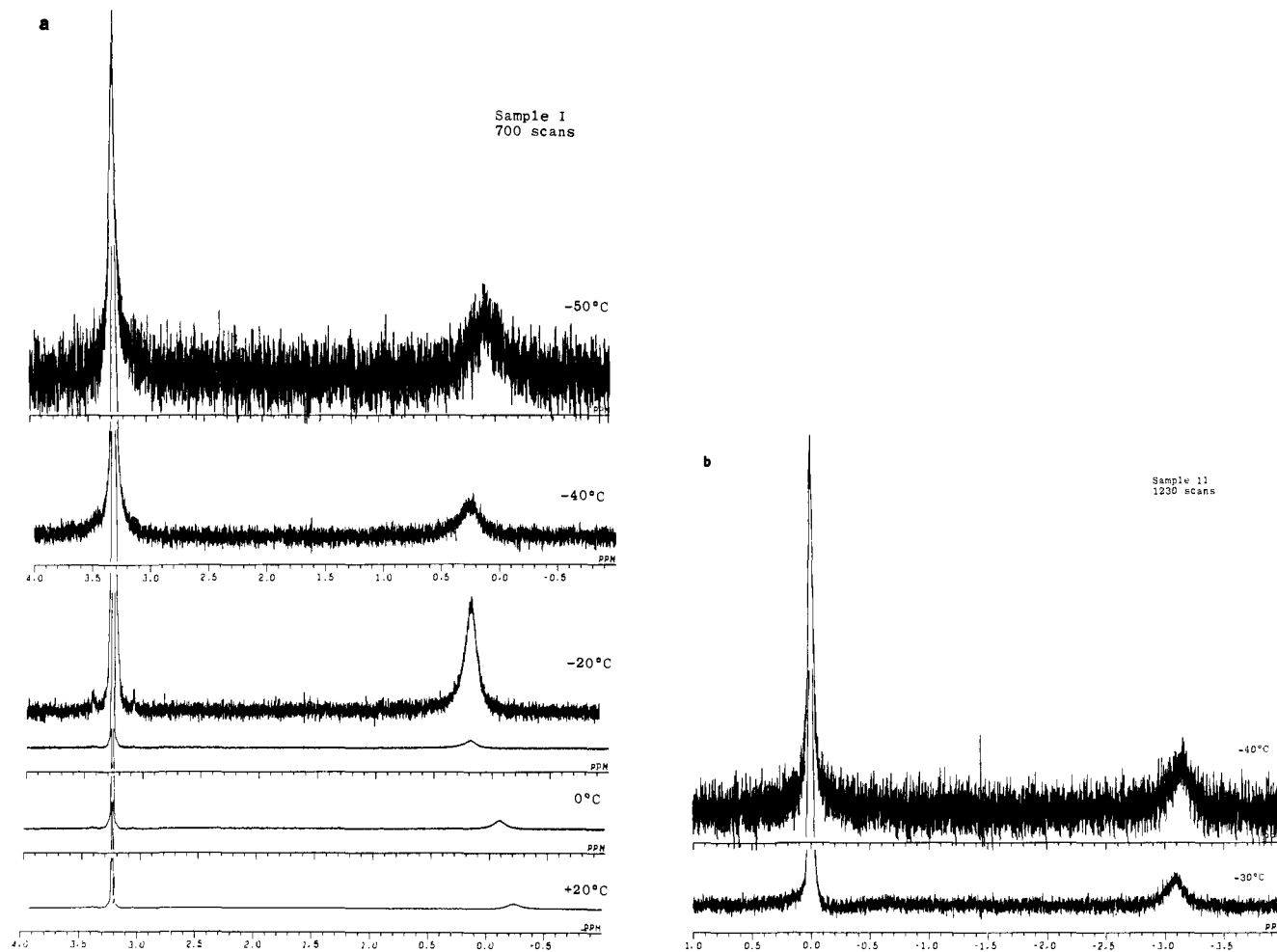
Figure 3. NMR spectra recorded with JEOL GX400 at the Institute for Molecular Science, operating at 399.97 MHz.
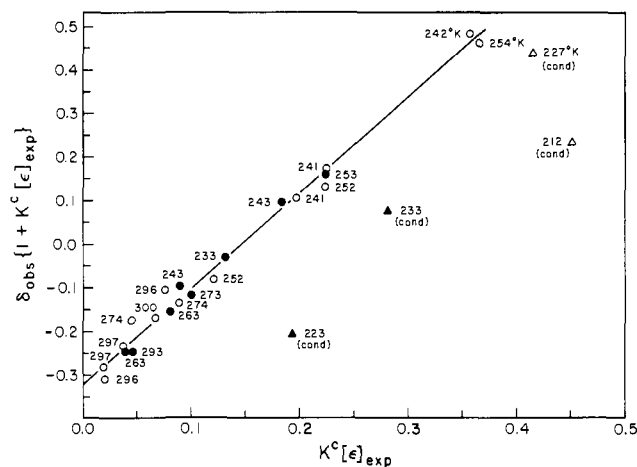

Figure 4. Graph of reduced data. Open points were derived from Cornell data and solid points from IMS. The triangles denote samples which partially condensed.

kcal/mol); at 223 K, $p \approx 4.7$ torr ($\Delta H_{vap} = 7.16$ kcal/mol); at 212 K, $p \approx 1.3$ torr ($\Delta H_{vap} = 7.34$ kcal/mol).

Thermochemical and Rate Calculations

For an RRKM estimate a k_d we need, in addition to the geometrical structures, the vibrational frequencies of the H-bonded complex and of the postulated transition species. In Table II we listed in the first column the assigned frequencies for the dimethyl ether,[5] for comparison with the second column which is a list of the molecular frequencies assigned to $(H_3C)_2O:HCl$.[6] The five new frequencies present in the complex are based both on directly observed fundamentals and analyses of combination bands. We
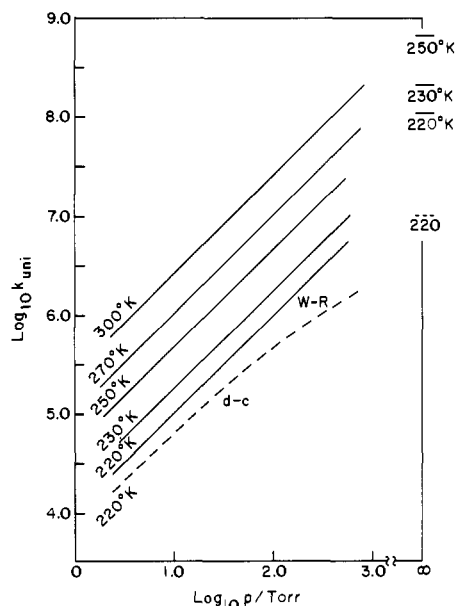

Figure 5. k_{uni} vs. p for various temperatures calculated via RRKM. The solid lines were obtained with the Whitten–Rabinovitch state count. For the dashed line, a direct count program was used.

soon discovered that Bertie and Falk's rough estimate of $\nu_\beta \approx 50$ cm^{-1} (based on their assignment of combination bands) is much too low. With that value the calculated $\Delta S° = -22.5$ eu. However, when we set $\nu_\beta \approx 100$ cm^{-1}, the calculated $\Delta S° = -25.2$ eu, in acceptable agreement with the experimental value (-25.6 eu). This calculation serves to check the permissable magnitudes for

Table II. Molecular Frequencies (cm^{-1})

	(CH$_3$)$_2$O		adduct	activated species	HCl
$\nu_{(C-O)}$	928		912	922	
	1102		1097	1100	
$\delta_{(COC)}$	418		415	417	
$\nu_{(C-H)}$			2996 (2)		
			2817 (2)		
			2952		
			2925		
$\nu_{(HCH)}$			1470 (3)		
			1456 (3)		
$\omega_{(H_3C-O)}$			1244		
			1150		
			1227		
			1179		
$\tau_{(H_3C+O)}$	160		165	160	
	270		275	270	
		$\nu_{(H-Cl)}$	2480	2725	2886
		$\nu_{(O\cdots H)}$	119	reaction coord	
		$\nu_{(O\cdots H-Cl)}$	525	100	
			470	100	
		$\nu_{(O\cdots H-Cl)}$	100	25	
			100	25	
	$\sigma = 2$		$\sigma = 1$	$\sigma = 1$	
	37 161.4		5 497 376.7	13 642 781.6	$I_x \cdot I_y \cdot I_z/$ AMU·Å^2

the low frequencies of the complex. We treated the torsional motions of the methyl groups as harmonic vibrations in both the free and bonded ether. Since their torsional frequencies are so nearly equal, the errors in the partition function due to the actual presence of hindered rotators cancel.

We assumed that the transition species is like the complex but with the O···HCl distance stretched to 1.5 times its equilibrium value, and with the frequencies of the ether and the HCl moieties midway between the free and bound states. The four low frequencies remain to be assigned. We reduced the corresponding values in the complex by amounts comparable to those used by

Lin and Laidler[12] (their model I) in their analysis of the thermal dissociation of ethane. For an approximate calculation we set $E°$ = $-\Delta H°$ and plotted the resulting $k_{uni}(p;T)$ vs. log p/torr in Figure 5. In the conventional RRKM program we assumed that the bath species consisted entirely of (H$_3$C)$_2$O:HCl, with a collision diameter of 7.5 Å and with unit de-excitation efficiency; the Whitten–Rabinovitch state count algorithm was used. The dashed curve for 220 K was recalculated by using a "direct count" program,[13] with the frequencies allocated to seven groups. It is immediately evident that even at a total pressure of 500 torr the *kinetics follows the low pressure limiting rate*, as expected. One could cogently argue that for the mixtures actually tested, better estimates of the rates would be an order of magnitude lower than those plotted, by allowing the smaller de-excitation collision radii with the free ether and acid, as well as less-than-unit de-excitation efficiency per collision.

Conclusions

Our experiments indicate that the rates of association/dissociation of this model hydrogen bond are too fast for measurement via gas-phase NMR. Consider our data at 223 K and assume $k_{uni} \approx 5 \times 10^4$, appropriate for a total gas density (corrected for condensation) of 5.8×10^{-6} mol cm^{-3}. Our experiments require that $k_d > 4.46 \times 10^3/[1 + 1.44 \times 10^5\{5.5 \times 10^{-6}\}] = 2.49 \times 10^3$. Hence, if the NMR method could measure rates faster by at least one order of magnitude, direct confirmation of the RRKM predictions might have been possible. It is conceivable that $E° > \Delta Hf°_{diss}$; these data impose an upper limit, $E° < 8.5$ kcal/mol. That these kinetics are in the second-order regime is not generally appreciated; $k_{bi}(223$ K$) > 4.29 \times 10^{+8}$ mol^{-1} cm^3 s^{-1}. Thus, the association step requires immediate stabilization by a third body.

Registry No. (CH$_3$)$_2$O, 115-10-6; HCl, 7647-01-0.

(12) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 79 (1968).
(13) Written by Professor E. R. Grant.