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NMR Spectroscopy of Cyclohexane. Gas-Phase Conformational Kinetics

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Abstract: Gas-phase ^1H NMR spectra of cyclohexane display dynamic line-shape effects which are both temperature and pressure dependent. Gas-phase inversion rates are slower and activation parameters are higher than those observed for liquid-phase samples. At 253 K chair–chair inversion rates range from 309 to 1290 s^{-1} for samples containing 1 torr of cyclohexane and from 100 to 2500 torr of SF_6. The gas-phase unimolecular activation parameters for the chair to transition-state reaction are $E_{act}(\infty)$, 12.5 (5) kcal/mol; $\Delta H^{\ddagger}$, 12.1 (5) kcal/mol; $\Delta G^{\ddagger}$, 10.4 (2) kcal/mol; and $\Delta S^{\ddagger}$, 5.7 (5) eu. The bimolecular activation energy is 11.2 (5) kcal/mol. The large value of $\Delta S^{\ddagger}$ and the difference between the unimolecular and bimolecular activation energies are consistent with proposed freely pseudorotating transition-state models. The pressure dependence of the inversion rate agrees with RRKM calculations assuming a freely pseudorotating transition state, indicating stochastic intramolecular vibrational relaxation in cyclohexane as ca. 11.5 kcal/mol, where there are ca. 1300 vibrational states per cm^{-1}. The phase dependence of $\Delta G^{\ddagger}$ ($\Delta G^{\ddagger}$(gas) − $\Delta G^{\ddagger}$(liquid) is ca. 300 cal) is consistent with a negative activation volume.

Although gas-phase NMR studies can provide kinetic information of comparable quality to that obtained for condensed phase samples and without solvent perturbations,[1-3] conformational studies using dynamic NMR (DNMR) as a kinetic probe have almost exclusively addressed processes occurring in the liquid phase.[4] In a recent communication we reported the gas-phase activation parameters for the ring inversion of cyclohexane, which are significantly higher than those obtained in liquids.[1] In the present paper we address the gas-phase kinetics of the isomerization process which is sensitive to the rate of intramolecular vibrational relaxation in this molecule.

Considerable experimental[5-16] and theoretical[5,6,17-25] work has recently been aimed at detailing the molecular conditions associated with the onset of stochastic intramolecular vibrational relaxation. Whether intramolecular vibrational relaxation in cyclohexane is statistical at internal energies of ca. 11–12 kcal/mol can be probed through measurement of the pressure dependence of the rate constants associated with the inversion process. For any unimolecular process the pressure dependence of the transition from bimolecular to unimolecular kinetics is a measure of the rapidity of intramolecular vibrational relaxation in the system.[26] Pressure-dependent rate data may be obtained convieniently for small- and medium-sized molecules which undergo NMR distinguishable unimolecular processes with moderate activation energies, ca. 5–20 kcal/mol. Systems in this energy regime are especially interesting because their vibrational-state density is much lower, ca. 35–3.5 × 10^4 states per cm^{-1}, than that of molecules undergoing chemical reactions which are almost always found to follow RRKM kinetics at state densities exceeding 10^6 per cm^{-1}.[26]

Our previous study of pseudorotation is sulfur tetrafluoride[3] demonstrated that intramolecular vibrational relaxation in this small molecule is significantly slower than that predicted by RRKM theory at internal energies of ca. 12.5 kcal/mol, where there is a 0.02-cm^{-1} spacing between vibrational energy levels. Cyclohexane undergoes a NMR differentiatable process with an activation barrier of similar energy to that of sulfur tetrafluoride. However, cyclohexane is a larger molecule with many more low-frequency vibrational modes which produce a state density of ca. 1300 per cm^{-1} near the zero-point-energy difference, ΔE_0, between the transition state and the equilibrium chair conformation. The present study compares details of the falloff behavior of cyclohexane isomerization rates to RRKM calculations in order to determine if this higher state density is sufficient for statistical intramolecular vibrational relaxation.

The transition state for the cyclohexane inversion process has been investigated by using several theoretical techniques. Studies by Pickett and Strauss[27] using a force field constructed from vibrational and structural data concluded that the transition state is freely pseudorotating and therefore has a much larger vibrational partition function than the equilibrium chair conformation. Semiempirical molecular orbital calculations are also consistent with an essentially freely pseudorotating transition state.[28] These calculations, however, predict inversion barriers of ca. 6–7 kcal/mol,[28,29] considerably lower than the values reported in previous liquid-phase NMR studies, ca. 10 kcal/mol,[30-34] and

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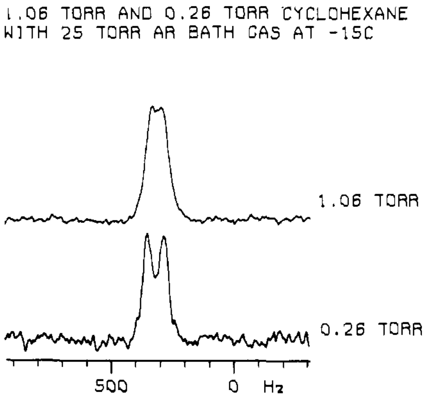

Figure 1. Gas-phase ^1H NMR spectra of cyclohexane–argon mixtures at 258 K. Spectra are Fourier transforms of the sum of ca. 200 transients. (a) 1.06 torr of cyclohexane and 25 torr of Ar; (b) 0.26 torr of cyclohexane and 25 torr of argon.

calculated by using ab initio techniques.[35] Predictions of a freely pseudorotating transition state for cyclohexane ring inversion have not been verified experimentally in DNMR studies of condensed-phase samples. Gas-phase experiments are more sensitive to the nature of the transition state since the difference between the unimolecular and bimolecular activation energies and the pressure dependence of the falloff as well as the entropy of activation can be obtained. Liquid-phase studies can only determine an activation entropy which may include a sizable contribution from solvent effects.

The present study also provides information pertinent to solvent perturbations on the conformational dynamics in this nonpolar system. A previous study of the phase dependence of the kinetic parameters associated with internal rotation in *N,N*-dimethyltrifluoroacetamide demonstrated faster gas-phase rates and lower activation parameters consistent with expected solvent internal pressure effects upon a process with a large positive activation volume, $\Delta V^{\ddagger}$.[2] The present study of cyclohexane obtains gas-phase rates which are slower and corresponding activation parameters which are higher than those previously obtained from liquid-phase measurements. These observations are consistent with expected solvent internal pressure effects on a process with a negative $\Delta V^{\ddagger}$.

Experimental Section

All NMR measurements were performed on a Nicolet 200-WB spectrometer with a 12-mm proton probe. Samples were contained in 12-mm Pyrex NMR tubes. Spectra were obtained with spinning samples and were acquired in an unlocked mode. Acquisition times were typically 1 s per transient. Typically 300 to 500 transients were collected at each temperature and their sum was stored in 8K of memory. All free induction decays were zero-filled prior to Fourier transformation. The resulting spectra as shown in Figure 1 have signal/noise ratios of at least 50/1. Samples were allowed to equilibrate for at least 10 min at each temperature prior to spectral acquisition. The temperature was measured between 173 and 423 K with use of a copper–constantan thermocouple placed in an empty non-spinning 12-mm NMR tube and was found to be constant within the active volume of our gas-phase samples. Thermocouple readings were used to calibrate the spectrometer temperature control settings over the experimental temperature range.

The low volatility of cyclohexane, 1 torr at 228 K, necessitated addition of an inert bath gas in order to perform pressure-dependent studies over a useful pressure range. SF_6 was chosen because of its high collisional efficiency and volatility and for purity considerations. Aldrich gold label (99+%) cyclohexane and instrument grade (99.99% min) sulfur hexafluoride (SF_6) were used in this study. All samples studied contained 1.00 torr of cyclohexane in addition to various amounts of SF_6 and will subsequently be referred to only by the partial pressure of SF_6 in each sample when it was prepared at 298 K. All pressure measurements were made with a MKS Baratron capacitance manometer with a 1000-torr head equipped with a digital readout. Samples with SF_6 pressures above 1 atm were prepared by quantitatively transferring samples of known pressure and volume into the NMR tubes. Sample tubes were attached to the vacuum line with $^1/_8$ in. o.d. capillary tubing. After the sample tubes were filled, the samples were frozen in liquid nitrogen and the tubes were sealed with a torch. Pressures were corrected for the residual volume after sealing and a 2% uncertainty results from this sample-preparation technique.

Rates were calculated with the program DNMR3-IT2 which uses a non-linear least-squares regression analysis to obtain the best fit of the experimental spectrum.[36] Typically 100–200 experimental points were used in the analysis of each spectrum. The shape of exchange-broadened NMR spectra is dependent on T_2, the effective line-width parameter, the limiting frequency shift between the two magnetically inequivalent sites, spin–spin coupling constants, and the exchange rate. The effective line-width parameter, T_2, was obtained for each sample studied. Inhomogeneity and relaxation contributions to the exchange-broadened line widths were estimated from high-temperature (323–423 K) data. At 323 K, exchange contributions to line widths are minimal since rates for all the pressures studied exceed 40 000 s^{-1}. For each sample, the effective line-width parameter was extrapolated from high-temperature line-width data, obtained from 325 to 375 K, which typically comprised 5 data points per sample, assuming a linear temperature dependence. For pressures above 500 torr high-temperature line widths are determined by field inhomogeneity. Below 500 torr relaxation is the major contributing factor, based on inversion-recovery experiments. The limiting axial–equatorial chemical shift difference in the gas phase is 89.2222 Hz (0.4460 ppm) and is independent of bath-gas pressure. This value is slightly smaller than that obtained by using a 251-MHz instrument at 173 K for a 1% solution of cyclohexane in CS_2, 0.4755 ppm.[32]

The complexity of the cyclohexane 12-spin system has to date precluded rigorous rate analyses.[4] Above coalescence cyclohexane ^1H NMR spectra can be analyzed by using a simple AB model.[37] Rates were calculated by totally neglecting coupling effects and also by using a single 13.05-Hz geminal coupling constant.[38] Both models yield rates which are identical within our uncertainties for data in the fast-exchange temperature range studied. Neglect of the other smaller coupling constants introduces a small systematic error in the rates obtained above coalescence and results in activation parameters slightly lower (1–2%) than their actual values.[37] Estimated errors arising from this simplified analysis were propogated and are included in our reported uncertainties.

Rates obtained from our exchange-broadened spectra have 5–10% associated uncertainties for spectra ca. 10–15 K above coalescence and ca. 20% associated uncertainties for spectra more than 30 K above coalescence due to estimated uncertainties in T_2, uncertainties in the position of the limiting proton resonances, the spectral signal/noise ratio, and the simplifying approximations inherent in our analysis.

The temperature dependence of the rates was used to determine activation energies in the customary way.[2] Results are reported at the 95% confidence limit.

Results

Since cyclohexane has 12 equivalent protons, good quality NMR spectra are obtainable with sample pressures as low as 0.1 torr. Figure 1 displays spectra of cyclohexane at 1.06 torr and 0.26 torr in samples which also contain 25 torr of Ar. These spectra demonstrate the sizable pressure dependence of the inversion rates. Varying the argon pressure by ca. 50 torr is found to have a similar effect on the rates as varying the cyclohexane pressure by 0.75 torr.

In order to obtain rates under both bimolecular and unimolecular kinetic conditions it was necessary to perform experiments in the presence of a bath gas with a high collision efficiency. The relative collision efficiencies of cyclohexane and SF_6 were estimated by measuring axial–equatorial proton exchange rates in samples containing varying amounts of cyclohexane and SF_6. A relative collision efficiency, $\beta_c \approx 0.95$ at 263 K, for SF_6 is estimated,[39] indicating that SF_6 has a collisional efficiency roughly comparable to cyclohexane.

Typical gas-phase NMR spectra of cyclohexane in SF_6 are shown in Figure 2. Spectra for both the high- (2500 torr) and low- (100 torr) pressure samples at 223 K show the axial and equatorial protons clearly resolved. At higher temperatures dy-

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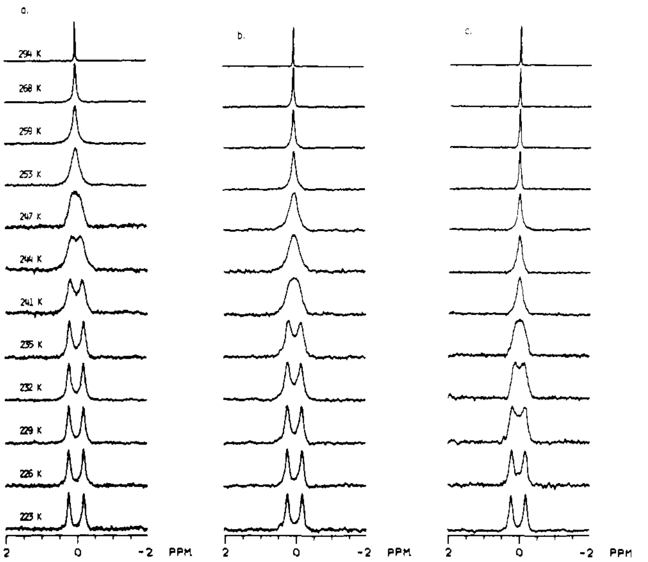

Figure 2. Gas-phase ^1H NMR spectra of cyclohexane–SF_6 mixtures. All samples contained 1.00 torr of cyclohexane and varying amounts of SF_6. (a) Temperature-dependent spectra at 98 torr. (b) Temperature-dependent spectra at 300 torr. (c) Temperature-dependent spectra at 2500 torr.

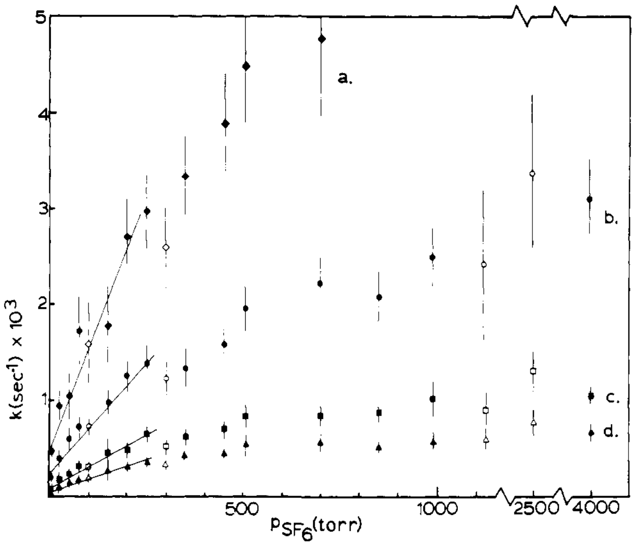

Figure 3. (a) Dependence of cyclohexane inversion rates on added SF_6 pressure at (a) 273 K, (b) 263 K, (c) 253 K, and (d) 248 K. Open symbols correspond to data interpolated for these temperatures from Arrhenius plots.

namic line-shape effects are apparent and are strongly pressure dependent. These spectra demonstrate that the activation energy is lower in the 100-torr sample since its associated exchange rates are less temperature dependent than those observed for the 2500-torr sample.

Figure 3 displays the pressure dependence of cyclohexane exchange rates at 273, 263, and 253, and 248 K. For this system both bimolecular and unimolecular rates are observed. The exchange reaction follows bimolecular kinetics up to ca. 200 torr at all four temperatures. Above ca. 500 torr the observed kinetics is unimolecular and the rates are independent of pressure within our experimental uncertainty. On the basis of these results samples containing 1 torr of cyclohexane and 2500 torr of SF_6 and those contaning 1 torr of cyclohexane and 98 torr for SF_6 were used to obtain unimolecular and bimolecular activation parameters. The temperature dependence of the exchange rates in these samples has been described previously.[1] Limiting high-pressure gas-phase exchange rates for cyclohexane ring inversion are approximately three times slower than corresponding rates observed in the liquid phase. Table I contains cyclohexane axial–equatorial exchange rates for our pressure- and temperature-dependent data. Table II contains our experimentally determined activation parameters and those previously reported for condensed-phase samples.[30–33]

Table I. Cyclohexane Chair–Chair Inversion Rates

$P(SF_6)$[a] (torr)	k (s^{-1}) 273 K	k (s^{-1}) 263 K	k (s^{-1}) 253 K	k (s^{-1}) 248 K
5.9	475 (59)	215 (25)	70 (26)	22 (20)
24.9	945 (154)	390 (50)	170 (20)	98 (24)
48.0	1040 (240)	490 (120)	240 (30)	150 (30)
72.0	1710 (360)	720 (100)	310 (50)	190 (30)
98.4[b]	(1570 (390))[f]	(720 (60))	(310 (30)	(200 (20))
149.7	1784 (390)	980 (110)	440 (170)	290 (30)
204.6	2732 (380)	1250 (150)	490 (70)	340 (30)
249.8	2980 (340)	1400 (170)	550 (70)	360 (40)
300.5[c]	(2620 (450))	(1220 (150))	(530 (60))	(340 (40))
343.6	3350 (390)	1340 (200)	620 (60)	430 (30)
449.3	3880 (520)	1600 (140)	690 (50)	460 (30)
513.3	4470 (560)	1960 (240)	830 (120)	540 (90)
692.8	4730 (800)	2230 (270)	840 (90)	560 (80)
847.5	6100 (950)	2080 (250)	860 (70)	510 (40)
987.4	6500 (980)	2500 (290)	1010 (180)	590 (90)
1140[d]	(5610 (950))	(2410 (800))	(970 (230))	(600 (80))
2500[e]	(8140 (930))	(3380 (760))	(1310 (200))	(790 (110))
4000	7330 (840)	3110 (350)	1050 (80)	660 (80)

[a] All samples contained 1.00 torr of cyclohexane and various amounts of SF_6. [b] Additional rates for the 98.4 torr of SF_6 plus 1.0 torr of cyclohexane sample are (T (K), s^{-1}): (247, 190 (20)); (250, 230 (25)); (253, 310 (30)); (256, 390 (30)); (259, 460 (40)); (262, 640 (70)); (265, 820 (80)); (268, 1160 (160)); (271, 1470 (170)); (274, 1730 (250)); (277, 2430 (440)); (280, 2980 (660)); (283, 3500 (1080)); (286, 3930 (860)); (289, 5025 (780)). [c] Additional rates for the 300.5 torr of SF_6 plus 1 torr of cyclohexane sample are (T (K), s^{-1}): (241, 190 (30)); (244, 238 (20)); (247, 300 (50)); (250, 400 (40)); (253, 560 (60)); (256, 660 (100)); (259, 940 (130)); (262, 1200 (150)); (265, 1380 (220)); (268, 1800 (320)); (271, 2160 (370)); (274, 2960 (450)); (277, 3680 (400)); (280, 3870 (530)); (283, 4940 (970)); (286, 6180 (2100)). [d] Additional rates for the 1140 torr of SF_6 plus 1 torr of cyclohexane sample are (T (K), s^{-1}: (229, 66 (20)); (232, 110 (30)); (235, 160 (20)); (236, 170 (27)); (237, 190 (20)); (238, 220 (30)); (241, 280 (40)); (244, 390 (60)); (247, 550 (60)); (250, 720 (70)); (253, 960 (150)); (256, 1330 (170)); (259, 1680 (300)); (262, 2240 (330)); (265, 2650 (310)). [e] Additional rates for the 2500 torr of SF_6 plus 1 torr of cyclohexane sample (T (K), s^{-1}) are: (235, 200 (26)); (238, 270 (30)); (241, 380 (60)); (244, 440 (40)); (247, 670 (100)); (250, 910 (160)); (253, 1290 (200)); (256, 1830 (280)); (259, 2520 (390)); (262, 3460 (760)); (265, 4860 (940)); (268, 9070 (1140)). [f] The numbers in parentheses refer to rates interpolated from Arrhenius plots.

Table II. Activation Parameters for Cyclohexane Ring Inversion

1 torr of gaseous cyclohexane + SF_6	E_{act} (kcal/mol)	$\Delta G^{\ddagger}{}_{298}$[e] (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
2500 torr SF_6	12.54 (47)	10.24 (40)	12.06 (47)	5.7 (5)
1100 torr SF_6	12.05 (27)			
300 torr SF_6	10.93 (50)			
100 torr SF_6	11.22 (47)			
liquid				
10% in CS_2[a]		10.2	10.8	2.8
1% in CS_2	10.20 (20)	10.08 (20)	10.30 (20)	0.6 (6)
c		10.1	11.51 (29)	4.6 (1.3)
liquid crystal[d]		10.15	10.3	0.5

[a] Reference 31. [b] Reference 32. [c] Reference 33. [d] Reference 34. [e] All parameters are calculated for the chair to transition-state reaction.

Discussion

Gas-phase thermal rate data for cyclohexane can be used to probe kinetic questions concerning rates of intramolecular vibrational relaxation and the nature of the transition state. Also direct comparison of gas-phase and liquid-phase data allows the direction and extent of solvent effects to be elucidated. These topics are discussed sequentially below.

For a unimolecular process, the pressure at which the transition between bimolecular and unimolecular kinetics occurs is a measure of the rapidity of intramolecular vibrational relaxation in critically energized molecules.[26] The falloff curves for cyclohexane which are shown in Figure 3, which display the rate constant as a function of bath-gas pressure, can be characterized by the pressure at which the observed rate has fallen to one-half of its limiting high-pressure value, $P_{1/2}$. At all four temperatures $P_{1/2}$ is ca. 200 torr, indicating that vibrational relaxation is occurring in this system on a subnanosecond time scale. For this system, the average time between hard sphere collisions at 200 torr is ca. 5×10^{-10} s. In order to ascertain whether this indicates ergodic behavior it is necessary to compare these results to model calculations. Limiting rates and also rates within the falloff and bimolecular regions were calculated in the formalism of RRKM theory.[40,41] Rotational constants determined from analysis of rotational fine structure on infrared absorbances and vibrational frequencies reported by Takashi et al. were used to characterize the equlibrium chair configuration.[42] The transition-state model proposed by Pickett and Strauss was used.[27] The most dramatic frequency difference associated with this model is a free pseudorotation with a 2.274-cm^{-1} internal-rotation constant. For this model, three ring-bending frequencies, 293, 430, and 458 cm^{-1}, are also different than those observed experimentally in the equilibrium configuration, 384, 427, and 427 cm^{-1}. The larger partition function associated with this transition state is due almost entirely to the high density of states associated with the pseudorotation, however. Pickett's force field, which was derived from vibrational and geometrical data, yields a zero-point-energy difference, ΔE_0, between the transition state and the chain conformer of 14.08 kcal/mol which is considerably higher than our experimental number. However, the authors note that experimental error in their force constants could lead to a 3–4 kcal/mol error in the transition-state energies bu the flatness of the pseudorotation path is not sensitive to the uncertainty in the force constants.[27]

In order to calibrate our calculational procedure, initial RRKM calculations were performed by using the vibrational frequencies and threshold energy obtained by Pickett et al. Our limiting high-pressure unimolecular rates obtained in this case at pressures above 1000 torr are identical with those calculated by Pickett et al. with use of transition-state theory. Rates in the falloff and bimolecular region were obtained by solving the equation

$$k_{\text{uni}} = \int_0^\infty \int_0^\infty \frac{k_a(E^*_v, E^*_r) P(E^*_v) P(E^*_r) \, dE^*_v \, dE^*_r}{(1 + k_a(E^*_v, E^*_r)/w)} \tag{1}$$

where $P(E^*_r)$ and $P(E^*_v)$ are the Boltzman distributions, $P(E^*_v) = N(E^*_v) \exp(-E^*_v/kT)/Q_v$ and $P(E^*_r) = N(E^*_r) \exp(-E^*_r/kT)/Q_r$ where $N(E^*_v)$ and $N(E^*_r)$ are the densities of vibrational and rotational quantum states, respectively, Q_v and Q_r are the molecular vibrational and external rotational partition functions, k_a is the energy-dependent microscopic rate, and w is the collision frequency.[41] This equation was solved for our system by exact numerical integrations. A hard-sphere-collision diameter of 5.34 Å was used to obtain the collision frequency in these falloff calculations. The hard-sphere diameter of SF_6 is slightly smaller, 5.01 Å, than that of cyclohexane, 5.67 Å at 300 K.[43] Since most collisions of cyclohexane in the dilute gas mixtures used are with SF_6, a mean effective diameter was used. Varying the collision diameter by 1 Å has little effect on the curvature or displacement of the calculated reduced falloff curves. Vibrational state densities were calculated for zero-point-energy (i.e., threshold) differences, ΔE_0, of 11.22, 11.72, and 12.22 kcal/mol. Vibrational-state densities range from 875 to 1855 states per cm^{-1} for energies from 11.22 to 12.22 kcal/mol, respectively. The vibrational sums are ca. 24 for the transition state evaluated 100 cm^{-1} above E_0.

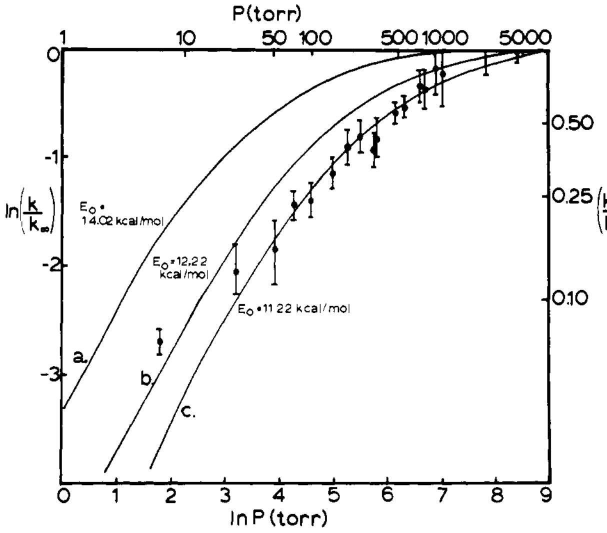

Figure 4. Experimental and calculated (see text) rate constants for cyclohexane inversion at 263 K: (O) experimental data. (a) RRKM calculation for $E_0 = 14.02$ kcal/mol. (b) RRKM calculation for $E_0 = 12.22$ kcal/mol. (c) RRKM calculation for $E_0 = 11.22$ kcal/mol.

Our experimental bimolecular activation energy is 11.22 (47) kcal/mol. The calculated associated zero-point-energy difference is 11.72 (50) kcal/mol, using the vibrational frequencies of Takahashi[42] for the conformer and Pickett et al.'s model for the transition state.[27] Falloff behavior was calculated for a range of zero-point-energy differences which reflect our experimental uncertainty limits. Figure 4 displays results of these calculations at 263 K. The logarithim of the ratio of the unimolecular rate to the limiting rate is plotted vs. the logarithim of the pressure of SF_6 in the sample. The experimental $P_{1/2}$ value of ca. 250 torr is reproduced by these calculations. With a zero-point-energy difference of 11.22, $P_{1/2}$ is 300 torr, and with a zero-point-energy difference of 11.72, $P_{1/2}$ is 205 torr. For Pickett's zero-point-energy difference of 14.08, $P_{1/2}$ is only 45 torr due to the larger internal energy content of the model.

Excellent agreement between the falloff behavior of the reaction which we observe experimentally and that calculated by assuming stochastic intramolecular vibrational relaxation is obtained. However, for this system, since several ring-bending modes may contribute to the reaction coordinate, the distinction between RRKM and Slater kinetics becomes blurred and the experimentally observed falloff behavior can be reproduced with a Slater model assuming 9–11 oscillators are contributing to the reaction coordinate.[44] For cyclohexane the six ring-bending modes do not contain contributions from other vibrational motions in the molecule according to the normal model analysis[42] making this large oscillator number improbable.

Several features of our results are consistent with the freely pseudorotating transition-state model[27] or one of comparable large degeneracy. Since cyclohexane does display stochastic or very nearly stochastic intramolecular vibrational relaxation, it is valid to calculate Eyring parameters associated with the reaction from unimolecular rate constants. The activation parameters were calculated for the chair $\rightleftharpoons$ transition-state process with use of the observed rates. A value of $^1/_2$ for the transmission coefficient was used in all cases since the above results demonstrate the validity of the strong collision assumption. These parameters as shown in Table II demonstrate a large positive entropy, 5.7 (5) eu, for the chair to transition-state reaction which is comparable to the

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calculated value obtained for the freely pseudorotating transition-state model, ca. 3–4 eu.[27]. Previous liquid-phase activation parameters report smaller activation entropies. As discussed above, the pressure dependence of the rate constants can be correctly predicted with this model although the quality of this agreement is not unique. Replacing the pseudorotation vibration with a harmonic vibration having a 3×10^{-4} cm^{-1} energy level spacing will also yield our experimental entropy difference.[41] Also, we obtain a unimolecular–bimolecular activation-energy difference of roughly 4 kT, which is also consistent with a transition state with a much larger partition function than the equlibrium chair conformation. All these features of our experimental results are consistent with a transition state with a large state density relative to the equilibrium configuration.

Another interesting experimental result is the observed phase dependence of the kinetic parameters. Gas-phase unimolecular ring-inversion rates for cyclohexane are ca. 2–3 times slower and the activation parameters are slightly higher than those obtained in liquid-phase studies. $\Delta G^{\ddagger}$ for conversion of the chair conformation of cyclohexane to the transition state is 10.4 (2) kcal/mol in the gas phase and 10.1 kcal/mol in CS_2 solutions (see Table II). The observed phase dependence is compatible with a negative activation volume. The partial derivative of $\Delta G^{\ddagger}$, the free energy of activation, with respect to pressure, equals the activation volume, $\Delta V^{\ddagger}$ for the process.[45] The internal pressure of an ideal gas is zero and that of liquid CS_2 at 298 K, is 3714 atm.[46] With use of these values and a $\Delta G^{\ddagger}$ of 370 cal, a $\Delta V^{\ddagger}$ value of ca. −4 cm^3/mol is obtained. Recently, variable-pressure and -temperature NMR studies of cyclohexane in several solvents have revealed that interconversion rates increase with increasing applied external pressure. The pressure dependence observed over a pressure range of 1–5000 bars yields activation volumes, $\Delta V^{\ddagger}$s, ranging from −5.0 cm^3/mol for an acetone solution to −1.5 cm^3/mol for a $C_6D_{11}Cd_3$ solution.[47] These results are consistent with earlier limited-pressure liquid studies.[48] These results are also qualitatively consistent with the slower gas-phase inversion rates reported in the present study and demonstrate that even in the absence of strong electrostatic interactions, kinetic parameters of molecules undergoing conformational exchange can be strongly phase dependent.

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Na^+ and Li^+ Effects on the Photoreduction of Benzophenone: A Picosecond Absorption Study

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Abstract: Picosecond absorption spectroscopy has been used to examine solvent effects on the ion-pair exchange reaction between alkali perchlorates and the ion-pair intermediate formed in the photoreduction of benzophenone by aromatic amines. In acetonitrile, the dynamics of exchange with $NaClO_4$ and $LiClO_4$ are similar. In DME the rate of exchange is found to be independent of $NaClO_4$ concentration but dependent on $LiClO_4$ concentration. No exchange is observed in Me_2SO; only solvent-separated ion pairs are observed. For an acetonitrile solution of equimolar 15-crown-5 and $NaClO_4$, exchange between the salt and the benzophenone radical anion/amine radical ion pair is prevented. The picosecond absorption spectrometer used in these studies is described in detail. Raman spectroscopy is used to probe the interactions between the solvent and the salts. In addition ground-state interactions between the alkali cation and the ketone are examined by using IR absorption spectroscopy.

The influence of the alkali cations Li^+ and Na^+ on the reduction of carbonyl compounds has been the subject of extensive investigation.[1] The rates of reaction as well as the overall chemistry have been shown to be highly sensitive to the particular cation present. Generally, the effects of added salts are discussed in terms of their complexation with the carbonyl moiety. The actual participation of the cation in the dynamic details of the reaction has never been fully addressed. The basis for an understanding of the role of the cation in the overall reaction must reside, in part, in the further elucidation of ion-pair dynamics.[2] By applying picosecond transient laser spectroscopy to the study of the photoreduction of benzophenone by *N,N*-diethylaniline in the presence of Na^+ and Li^+, we have developed a new probe into ion-pair chemistry; one which we believe can lead to a greater understanding of the effects of alkali cations on carbonyl chemistry.

The existence of ion pairs was postulated by Bjerrum[3] in an attempt to explain the behavior of ionophores in solvents of low dielectric. Since then, several advances have been made in our understanding of ion-pair structure, the most notable being those by Winstein,[4] Fuoss,[5] Grunwald,[6] and Hogen-Esch and Smid.[7]

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