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# Conformational kinetics of methyl nitrite. I. NMR spectral evidence for statistical intramolecular vibrational redistribution

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Pressure dependent rate constants for syn=anti conformational exchange in gaseous methyl nitrite and in gaseous methyl nitrite– $CO_2$  mixtures have been obtained from line shape analyses of <sup>1</sup>H NMR spectra. The pressure dependence of the exchange rates is consistent with a specific reaction rate constant of  $\sim 1 \times 10^9$ /s which agrees with RRKM calculations demonstrating that intramolecular vibrational redistribution is occurring at the statistical limit in methyl nitrite molecules with  $\sim 12$  kcal/mol of internal vibrational energy. At 12 kcal/mol methyl nitrite has a state density of  $\sim 160/\text{cm}^{-1}$ . These results indicate strong anharmonic and/or Coriolis coupling between vibrational levels. Bimolecular rate data for methyl nitrite and methyl nitrite– $CO_2$  mixtures are consistent with a collisional efficiency  $\beta_p$  for  $CO_2$  of 0.95(8) for activation of syn–anti conformational exchange at 258.8 K.

# **I. INTRODUCTION**

This paper addresses the gas phase kinetics of conformational conversion in methyl nitrite (MEONO). Pressure dependent exchange rate constants obtained for pure MEONO gas and for mixtures of MEONO and carbon dioxide are compared to predictions assuming statistical intramolecular vibrational redistribution (IVR). A second paper delineates and discusses the phase dependence of rate constants and associated kinetic parameters.<sup>1</sup>

RRKM theory assumes, and experiment confirms, that for the vast majority of unimolecular reactions induced by collisional excitation, IVR rates greatly exceed specific reaction rates.<sup>2</sup> IVR rates in reacting molecules depend on the density of vibrational states evaluated at  $E_0$ , the threshold energy for the reaction and the magnitudes of appropriate anharmonic and Coriolis coupling matrix elements.<sup>3</sup> At typical threshold energies for unimolecular dissociations and isomerizations, state densities are typically  $10^{6}/\text{cm}^{-1}$ and even if coupling elements between these states are very small, IVR generally proceeds on a time scale many orders of magnitude faster than typical specific rate constants.<sup>4</sup> Under these conditions, specific reaction rates are correctly predicted by statistical theories. The opposite dynamical extreme occurs at much lower state densities. For small molecules at low levels of vibrational excitation, typical vibrational energy level spacings greatly exceed anharmonic and Coriolis coupling matrix elements and a zeroth order normal mode description applies to intramolecular vibrational dynamics. In this regime, vibrational redistribution requires collisions.5

Moderately sized molecules with energies between 8 and 20 kcal/mol have intermediate state densities of between 10 and 10 000/cm<sup>-1</sup>. A few experimental studies addressing IVR in moderately excited molecules have recently appeared. Infrared fluorescence studies of 23 representative molecules have demonstrated that collisionless intramolecular vibrational redistribution (IVR) occurs in molecules with only ~8.5 kcal/mol of excess vibrational energy,  $E_{n}$ .<sup>6</sup> In these studies, performed under collisionless conditions, molecules were initially excited into the v = 1 level of the C-H stretch and resonance fluorescence was monitored. Variations in the observed threshold densities for collisionless IVR were attributed to variations in the relative magnitudes of anharmonic matrix elements coupling the initially prepared state to the vibrational manifold. These results agree qualitatively with earlier studies where  $C_1 - C_4$  alkanes were initially excited in the v = 2 level of the C-H stretch and where a threshold density of 15 states/ $cm^{-1}$  was reported for the onset of collisionless IVR.7 No rate data were obtained in these studies. Although these studies clearly establish that rapid IVR does occur in molecules of moderate size at moderate levels of excitation, further information is needed to elucidate rates and the extent to which other vibrations contribute to the process.

Many unimolecular processes with activation energies of  $\sim$  5–20 kcal/mol which result in nuclear exchange between magnetically inequivalent sites can be studied using pressure dependent gas phase NMR spectroscopy.<sup>8-11</sup> Pressure dependent exchange rates can be compared with model calculations to yield information about IVR at internal energies required for a specific exchange process. From the pressure dependence of unimolecular rate constants for structural exchange reactions obtained from NMR line shape data, we have recently determined that IVR in cyclohexane<sup>8,9</sup> at 12.5 kcal/mol (1500 states/cm<sup>-1</sup>) occurs at the statistical limit whereas for SF<sub>4</sub> at 13 kcal/mol (70 states/cm<sup>-1</sup>) IVR occurs at rates which are slower than the statistical limit.<sup>10</sup> The reaction rates of critically energized cyclohexane and SF<sub>4</sub> molecules are  $\sim 2 \times 10^9$ /s and  $4 \times 10^8$ /s, respectively and RRKM predictions yield specific rate constants of  $\sim 10^{9}$ /s for cyclohexane and  $10^{10}$ /s for SF<sub>4</sub> which is a much smaller molecule. For  $SF_4$  it is interesting to note that the observed rates are slower than statistical predictions and are much slower than Slater type models which predict reaction to occur in the time frame of a single vibrational period.

MEONO has a vibrational state density of  $\sim 160/cm^{-1}$ 



FIG. 1. Syn and anti conformers of MEONO.

at 12 kcal/mol and at this energy undergoes the conformational process shown in Fig. 1. Most of the vibrational state density at this energy arises from the low frequency methyl and methoxy torsions. Assuming anharmonic couplings on the order of  $\sim 0.01$  cm<sup>-1</sup>, rapid intramolecular vibrational redistribution should occur and the present study was undertaken to provide additional insight into this process. An earlier study of gas phase conformational kinetics in MEONO has appeared but the poor quality of that data did not allow details of the falloff region to be established.<sup>12</sup>

### **II. MATERIALS AND METHODS**

# A. Sample preparation

The following chemicals were obtained from the sources indicated: tetramethylsilane (TMS) (Aldrich, NMR Grade) and carbon dioxide (CO<sub>2</sub>) (Liquid Carbonic, Grade A). The TMS and CO<sub>2</sub> were further pruified by five freezepump-thaw cycles. MEONO was synthesized from methanol (Mallinkrodt, spectrophotometric grade) and sodium nitrite (Mallinkrodt, analytical reagent) by dropwise addition of 50 ml of ice-cold 6N  $H_2SO_4$  (Mallinkrodt) to a stirred solution of 0.55 mol sodium nitrite in 0.50 mol methanol over a period of two hours. The reaction mixture was maintained at a temperature of 268 K. The light yellow product was collected in a dry ice/acetone trap over sodium bicarbonate (Mallinkrodt analytical reagent) and purified by vacuum distillation into a storage bulb followed by five freeze-pump-thaw degassing cycles. No detectable impurities were observed via GC analysis on an Analabs 6 ft SE-30 column with 4 min retention times, or with infrared or  ${}^{1}H$ NMR spectroscopy. Purified MEONO was stored without detectable decomposition under vacuum at 248 K over a six month period.

Gas phase NMR samples were prepared in 12 mm NMR tubes (Wilmad high precision, round bottom). Pressures were recorded on a MKS Baratron capacitance manometer with a 1000 Torr head and digital readout. A series of 34 gas phase samples, listed in Table I, was prepared at 298 K. Each sample was sealed with a torch and immediately immersed in liquid nitrogen to prevent reaction of the MEONO with the hot glass. No decomposition has been detected in samples prepared using the above procedure. Reported pressures have an uncertainty of  $\pm 0.5\%$ . A series of 30 samples (listed in Table IV) with total pressures of less than one atmosphere, containing 0.70 Torr TMS and 17.0 Torr MEONO and various partial pressures of CO<sub>2</sub> was prepared at 298 K as follows. The TMS and MEONO were introduced into the sample tubes by the procedure described above, followed by the introduction of CO<sub>2</sub>. At least 30 min were allowed for mixing prior to sealing each sample. A series of eight samples (list in Table I) containing more than one atmosphere of  $CO_2$  was prepared in heavy walled (12 mm o.d., 8 mm i.d. Wilmad special order) round bottom NMR tubes for reasons of safety. To offset the resulting loss in NMR signal, 2.7 Torr of TMS and 90 Torr of MEONO were introduced into each tube and condensed with liquid nitrogen. The  $CO_2$  was transferred quantitatively from a calibrated glass bulb into each NMR tube. The resulting samples were sealed with a torch. Appropriate corrections in the final volume of the NMR tube were taken into account in the calculation of the sample pressures.

#### **B. NMR measurements**

All NMR measurements were made with a Nicolet 4.8 Tesla wide bore FT spectrometer with proton observation at 200.067 00 MHz. All spectra were obtained on spinning samples in the unlocked mode. Under unlocked conditions, the total spectrometer frequency drift is less than 1 Hz over a 24 h period. Typical acquisition times for a sum of 300 transients were under 30 min, incurring a negligible drift contribution to the resulting natural linewidths. Temperatures were calibrated with a copper constantan thermocouple as described previously.<sup>1</sup> Temperatures were regulated to  $\pm$  0.1. All NMR spectra were acquired at 258.8 K.

Pressure dependent  $T_{1s}$  were determined using the inversion recovery method and were found to increase from  $\sim 0.4$  s at 100 Torr to several seconds at pressures above760 Torr.<sup>13</sup> All spectra were obtained with delay times in excess of 5  $T_{1}$  in order to prevent discrimination between conformers in the frequency domain spectra.

Gas phase transients were collected using a 12 mm proton probe. A pulse width of  $8 \mu s$  (60° flip angle) with a sweepwidth of  $\pm$  2000 Hz was used to acquire transients into 8 K of memory. Typically, pressures of MEONO above 200 Torr required acquisition and Fourier transformation of 100 transients into the frequency domain to produce spectra with signal/noise ratios greater than 500/1 in the fast and slow exchange limits and signal/noise ratios greater than 200/1 in the exchange broadened region.

Analysis of the exchange broadened spectra to obtain syn-anti interconversion rates was accomplished using the iterative analysis program DNMRS.<sup>14</sup> The best estimates of the syn and anti populations, limiting chemical shifts, transverse relaxation times, and the digitized experimental NMR spectra were used as input parameters. The temperature dependence of the syn and anti populations in the gas phase at the slow exchange limit has been determined, 15 and extrapolated to 258.8 K. In the gas phase, there is little temperature dependence to the limiting chemical shifts of both conformers, with  $v(syn) = 3.504_2$  and  $v(anti) = 4.570_5$  ppm. The transverse relaxation time,  $T_2$  was estimated for all exchange broadened spectra by measuring the FWHM of the methyl nitrite resonance at 193 and 423 K for each sample studied (where vapor pressure allowed at 193 K) and assuming a linear temperature dependence through the exchange broadened region. An estimation of the magnetic field inhomogeneity contribution to the effective  $T_2$  value was obtained from the FWHM of the TMS resonance at each temperature

Neat methyl nitrite gas		Methyl nitrite (15.3 Torr) + CO <sub>2</sub> mixtures		Methyl nitrite (90 Torr) + CO <sub>2</sub> mixtures	
* Pressure <sub>MEONO</sub> (Torr)	<sup>b</sup> k <sub>NMR</sub> (s <sup>-1</sup> )	*Pressure <sub>co,</sub> (Torr)	<sup>b</sup> k <sub>NMR</sub> (s <sup>-1</sup> )	° Pressure <sub>MEONO</sub> (Torr)	<sup>b</sup> k <sub>NMR</sub> (s <sup>-1</sup> )
4.80	50.9	12.9	65.4	929	297
7.12	42.4	19.3	72.5	1310	333
9.71	39.5	25.6	76.6	1650	334
13.0	40.2	32.2	83.0	1980	399
15.1	55.0	38.7	89.1	2450	391
18.2	53.6	44.9	93.1	3300	407
22.9	60.0	51.6	102	4340	410
26.8	69.7	58.4	111	7390	399
35.8	75.4	71.5	118		
44.8	83.2	84.3	123		
53.8	97.3	96.7	133		
63.3	104	109	140		
72.9	113	120	134		
82.6	120	142	155		
92.8	129	165	151		
103	138	189	164		
117	146	212	164		
131	154	241	181		
144	163	271	192		
158	173	302	194		
167	170	331	208		
180	180	363	225		
191	183	400	228		
205	190	429	236		
219	197	462	241		
232	194	503	248		
246	204	550	267		
259	205	602	271		
272	212	653	282		
286	216	701	267		
300	222				
324	227				
345	229				
364	234				
	4.77				

TABLE I. Pressure dependent exchange rates of methyl nitrite gas at 258.8 K.

\* Pressure at 298 K, uncertainties  $\sim 1\%$ .

<sup>b</sup> Uncertainties in exchange rate  $2\sigma \sim 5\%$ .

°Uncertainties ~4%.

for each sample. The inhomogeneity contribution, along with any sensitivity enhancement (usually between 1 and 3 Hz) was added into the estimate of  $T_2$  at each temperature for each sample. The digitalized NMR spectra consisted of 1000 frequency/amplitude ordered pairs obtained between ~6.60 and 1.47 ppm with a spacing of 0.976 562 5 Hz/ point. For each analysis, the limiting chemical shifts were allowed to vary within  $\pm 1$  Hz of the estimated value, the exchange rate was allowed to vary freely, and the transverse relaxation times and conformer populations were held fixed.

# **III. RESULTS**

The limiting chemical shift difference between the syn and anti methyl <sup>1</sup>H resonances of MEONO is 1.066 ppm, and with proton observation at 200 MHz accessible interconversion rate constants  $k_{NMR}$  determinable from line shape analysis, range from 10 to 1200/s. Exchange broadened spectra are observed at temperatures below ambient and sample volatility limitations necessitated additional measurements in the presence of a bath gas in order to completely characterize the pressure dependence of the exchange rate constants. Spectra of neat MEONO and of MEONO-CO2 mixtures were obtained. Since rates obtained from line shape analysis are most reliable in the intermediate exchange region, preliminary studies were performed to establish an optimum temperature for subsequent pressure dependent studies. At 258.8 K rates range from ~25 to 400/s with increasing pressure and falloff behavior can be completely characterized at this temperature. Representative exchange broadened <sup>1</sup>H NMR spectra of MEONO gas at 258.8 K appear in Fig. 2(a). At low pressures, the anti and syn resonances are resolved at 4.57 and 3.504 ppm, respectively. For this series of traces, calculated rates range from 50.9 to 234/s. Lineshapes at 272 and 363 Torr are noticeably different indicating that the limiting rate constants cannot be obtained for pure MEONO gas at its vapor pressure ( $\sim 380$ Torr) at 258.8 K.

Samples containing mixtures of MEONO and  $CO_2$ were used to obtain spectra in the high pressure region. Representative spectra shown in Fig. 2(b) were obtained for a constant MEONO pressure of 15.1 Torr and variable pres-



FIG. 2. Gas phases <sup>1</sup>H NMR spectra of MEONO at 258.8 K. Resonances at 3.504(2) and 4.57 ppm are assigned to *syn* and *anti* conformers, respectively; (a) neat MEONO gas. Labels refer to sample pressures at 298 K. Associated rates which range from 50.9 to 234 s<sup>-1</sup> for 4.28 to 363.8 Torr samples appear in Table I; (b) 15.3 Torr MEONO. Labels refer to the partial pressure of CO<sub>2</sub>. Associated rates which range from 65.4 to 400 s<sup>-1</sup> for PCO<sub>2</sub> of 12.9 to 7390 appear in Table I.

sures of  $CO_2$ . The pressure labels in Fig. 2(b) refer to the partial pressure of  $CO_2$ . The top four traces shown have associated rates of ~400/s for  $CO_2$  pressures ranging from 1310 to 7390 demonstrating that first order kinetics is operative at these pressures. Table I lists experimental rate constants for all samples and their associated uncertainties. Figure 3 displays the pressure dependence of inversion rates in pure MEONO gas and demonstrates that bimolecular rate data is experimentally obtainable up to pressure of ~150 Torr. At pressures below ~20 Torr, rates increase with decreasing pressure, most likely due to the increasing importance of wall collisions in our small sample tubes.

Of special interest is the transition pressure  $P_1$  the pressure at which the unimolecular rate constant has fallen to 1/2 of its infinite value. Using a value of  $k_{\infty}$  of 400/s,  $P_1$  occurs at 235 Torr for neat MEONO. At this pressure the collision

frequency is  $\sim 1 \times 10^9$ /s assuming a collision diameter of 3 Å and assuming that the rate of deactivating collisions is comparable to the rate of reaction of critically energized molecules. The transition pressure for MEONO-CO<sub>2</sub> mixtures is only slightly greater (230 Torr) than for pure MEONO indicating that the two gases have roughly equivalent collision efficiences.

In order to compare rate data of neat MEONO and rate data of MEONO-CO<sub>2</sub> mixtures, relative collisional efficiencies were calculated. Bimolecular rate data for neat MEONO and MEONO-CO<sub>2</sub> mixtures is shown in Fig. 4. The ratio of the slopes, obtained by weighted least squares regression analyses, yields a relative activating collision efficiency for CO<sub>2</sub>,  $\beta_p$  of 0.95(8). The collison efficiency of CO<sub>2</sub> for activating the *syn-anti* conformer conversion of MEONO is considerably higher than its relative efficiency for activation of unimolecular dissociations and isomerizations. For example,  $\beta_p$  for CO<sub>2</sub> for activating isomerization of methyl isocyanide at 553.8 K is 0.32.<sup>16,17</sup>

Comparisons between the results of model calculations and the experimental rates necessitated conversion of the MEONO-CO<sub>2</sub> sample pressures to an effective CO<sub>2</sub> pressure, since two sets of samples (Table I) were used. The effective pressure of CO<sub>2</sub> was calculated by multiplying the pressure of MEONO in the samples with pressure over one atmosphere by  $\beta_p^{-1}$  and adding it to the pressure of carbon dioxide in each sample. The pressure axes of the reduced plots in Fig. 5(a) and 5(b) incorporate these corrections.

# **IV. DISCUSSION**

We can compare the experimental falloff behavior obtained for syn-anti exchange in MEONO to model predictions and to previous results for other molecules. These topics will be discussed sequentially below. A high pressure activation energy,  $E_{act}$ , of 11.0(3) kcal/mol has been obtained previously for a sample containing 195 Torr of MEONO and 4100 Torr of Ar.<sup>1</sup> This sample is estimated to produce inversion rates 85% of their limiting values. This value is consistent with a threshold energy of  $\sim 12$  kcal/mol. Threshold pressures for syn-anti interconversion of MEONO are consistent with a specific rate constant for critically energized molecules of  $\sim 10^{9}$ /s. Comparison with model calculations can be used to probe the extent and rapidity of IVR in MEONO at  $\sim 12$  kcal/mol. At this energy, MEONO has a state density,  $\rho(e_0)$  of 160/cm<sup>-1</sup> calculated from recently reported vibrational frequencies<sup>18,19</sup> using a Rabinovitch-Setzer direct count procedure. At 11 kcal/mol  $\rho(e)$  is 100/cm<sup>-1</sup>.

For MEONO conformer exchange, the slowest possible specific rate assuming one reaction channel is  $c/p(e_0)$ , where c is the speed of light, or  $\sim 2 \times 10^8$ /s, significantly slower than our observed value.<sup>21</sup> The fastest possible specific rate for critically energized molecules occurs in the absence of IVR. In this case, only collisions which transfer energy into the reaction coordinate can result in chemical reaction. If the outcome of a collision was deposition of sufficient vibrational energy into the C–O torsional vibration, which is the reaction coordinate for *syn-anti* conversion and if vibrational relaxation cannot occur in the absence of collision, then the



FIG. 3. Pressure dependence of observed rate constants for pure MEONO gas at 258.8 K.

specific rate is simply related to the O-alkyl internal rotation vibrational period. The time for completion of one torsional oscillation is  $1.5 \times 10^{-13}$  s assuming a frequency of 224 cm<sup>-1</sup> which is the average of fundamental torsional frequencies obtained for *syn* and *anti* MEONO.<sup>18</sup> This model is consistent with extension of second order kinetics to very high pressures. A collision frequency of  $6.7 \times 10^{12}$ /s occurs at a pressure of  $\sim 1 \times 10^6$  Torr for this system. A model assuming no collisionless IVR is clearly incompatible with our experimental data.

Since preliminary analysis indicates rapid IVR in MEONO at internal energies of  $\sim 12$  kcal/mol, predictions using RRKM theory were also obtained and compared to

experimental falloff data to see if IVR is occurring at the statistical limit. The most sensitive input parameters in any RRKM calculation are the vibrational frequencies and the threshold energy.<sup>20</sup> Since we are modeling pressure dependent thermal rate data, kinetic diameters, which must be estimated, significantly effect results. The Arrhenius A factor, estimated from previously obtained temperature dependent rate data,<sup>1</sup> is consistent with a partition function ratio  $z^{\neq}/z_{conformer}$  of ~0.7. Vibrational frequencies for the syn conformer were used to calculate the conformer partition function and frequencies for the transition state were averages of the syn and anti forms. The methyl top frequency was varied in the transition state to match the experimental



FIG. 4. Syn  $\Rightarrow$  anti exchange rates for MEONO in the bimolecular region as a function of pressures at 258.8 K: •, neat MEONO pressures;  $\blacktriangle$ , partial pressure CO<sub>2</sub> in samples containing 15.5 Torr of MEONO gas. The relative collision efficiency of CO<sub>2</sub>,  $\beta c$  is 0.95(8) (see the text).

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FIG. 5. Reduced experimental and calculated rate constants for methyl nitrite conformer exchange at 258.8 K for samples containing MEONO and CO<sub>2</sub>. Pressures were converted to effective PCO<sub>2</sub> using  $\beta c = 0.95$ . Each experimental point is indicated by a  $\blacktriangle$ . (a) Calculations using a constant collision diameter of 3 Å and varying  $E_0$  from 10.5 to 13.5 kcal/mol. (b) Calculations using a constant  $E_0$  of 12.5 kcal/ mol and varying the collision diameter from 2.50 to 3.25.

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 $z^{\neq}/z_{conformer}$  ratio. As is generally found, calculations were found to be insensitive to the specific frequencies used, if the ratio  $z^{\neq}/z_{conformer}$  was maintained.<sup>22</sup> For a threshold of 12.0 Å. kcal/mol, k (e) is  $2 \times 10^9$ /s, close to the observed experimental value. RRKM specific rates were used to model the observed falloff behavior of the reaction. A falloff calculation was performed with 50 increments of integration with a spacing of 0.10 kcal.<sup>22</sup> Calculations were performed to deter-

spacing of 0.10 kcal.<sup>22</sup> Calculations were performed to determine the threshold energy and collision diameter dependence of model predictions. Results of these calculations appear in reduced plots shown in Figs. 5(a) and 5(b) for MEONO-CO<sub>2</sub> mixtures and in reduced plots shown in Figs. 6(a) and 6(b) for neat MEONO. Best agreement between ob-



FIG. 6. Reduced experimental and calculated rate constants for MEONO conformer exchange at 258.8 K for neat MEONO. Each experimental point is indicated by a  $\bullet$ . (a) Calculated falloff curves with a constant collision diameter of 3 Å varying  $E_0$  from 10.5 to 12.5 kcal/mol. (b) Calculated falloff curves with a constant  $E_0$  of 12.5 kcal/mol varying the collision diameter from 3.00 to 3.50 Å.

served and calculated rate constants is obtained for a threshold energy of  $\sim 12$  kcal/mol and a collision diameter of  $\sim 3$ Å. These values are consistent with the experimentally determined Eact for MEONO and with available cross section information. The hard sphere collision diameter of CO<sub>2</sub> is 3.7 Å at 300 K.<sup>23</sup> Hard sphere diameters decrease with increasing temperature<sup>24</sup> and we expect the hard sphere collision diameter of CO<sub>2</sub> to be slightly but significantly smaller at 258.8 K. A hard sphere collision diameter for MEONO has not been reported. Pressure dependent  $T_1$  measurements for MEONO are consistent with a rotationally inelastic collision diameter of 3.1 Å. Spin rotation cross sections are generally found to be 60%-80% of the value of hard sphere cross sections<sup>25</sup> and the observed spin rotation cross section for MEONO is consistent with a hard sphere diameter of  $\sim 4$ Å. The observed optimum 3 Å collision diameter for both pure MEONO and for CO<sub>2</sub> is compatible with a deactivation collision efficiency  $\lambda$  of ~0.7 which is reasonable. Reported  $\lambda$  's typically range from 0.1 to 1 for unimolecular reactions.<sup>2</sup>

These calculations demonstrate that the kinetics of synanti conformational exchange in MEONO is compatible with RRKM predictions for reasonable models. For the validity of statistical theories, the intramolecular vibrational redistribution rate  $k_{IVR}$  must exceed the reation rate k(e). IVR rates depend on state densities and anharmonic and Coriolis coupling matrix elements, according to

$$k_{\rm IVR} = \frac{2\pi}{\hbar} \left\{ \sum_{l} \rho_l(s) (Vsl)^2 \right\}$$

where  $\rho_l(s)$  is the density of states in manifold *l* evaluated at the energy of state *s*, and *Vsl* are the coupling matrix elements.<sup>26</sup> For our system, assuming a constant  $\rho_l(s)$  of 100/ cm<sup>-1</sup>,  $1 \times 10^9 \text{ s}^{-1} < \{2\pi/\hbar \ \rho_l(s) (Vsl)^2\}$  or  $\Sigma (Vsl)^2 > 0.03$ cm<sup>2</sup>. These results indicate that large anharmonic and/or Coriolis coupling matrix elements exist between vibrational states of MEONO. Although IVR rates are not directly determinable from thermal rate data, we can conclude that in this case IVR does occur and IVR rates exceed  $1 \times 10^9$ /s.

It is informative to compare the results of the present study with similar results obtained for systems which undergo NMR differentiable prosesses at different state densities. The observed pressure dependent behavior of cyclohexane  $(\rho(E_0); 1500/\text{cm}^{-1}; E_0 \sim 12.5 \text{ kcal/mol})$  is consistent with statistical IVR. It is especially interesting to compare the results obtained for SF<sub>4</sub> ( $\rho(E_0)$ ; 70/cm<sup>-1</sup>;  $E_0 \sim 13$  kcal/ mol) with those of MEONO. State densities at threshold differ by only a factor of 2 but RRKM predictions clearly do not apply in the SF<sub>4</sub> case.<sup>10</sup> Factors contributing to observed differences must include the nature of coupling between energy levels in these two systems. For MEONO the methyl and methoxy tops contribute appreciably to the state density. They are both A'' symmetry and can interact. For SF<sub>4</sub> the transition state has higher symmetry than the equilibrium configuration. It is probable that coupling can occur between a much smaller subset of vibrational states of SF<sub>4</sub> due to symmetry restrictions.

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