Conformational Characteristics of Methyl Nitrite: A Cryospectroscopic Study

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Mid-infrared spectra of solutions in liquid argon, krypton, and xenon of methyl nitrite, which occurs as a mixture of cis and trans conformers, have been investigated. In liquid argon and in liquid krypton at temperatures below 150 K, the rate of conformational equilibration is found to be negligible, while at temperatures above 160 K in liquid krypton, and in liquid xenon, the equilibration is near-instantaneous. The standard enthalpy difference $\Delta H°$ between the conformers in liquid krypton was measured in the 165−205 K interval to be 3.02(9) kJ mol^{-1}, with the cis as the more stable conformer. Starting from solutions containing nonequilibrium populations of the conformers, the conformational equilibration was studied as a function of time at five different temperatures between 150 and 160 K in liquid krypton. From these kinetic data, the extinction coefficient ratios for the ν_3 and ν_8 conformational doublets have been determined to be 1.2(2) and 4.8(8), respectively. The extinction coefficient ratio for ν_8 was combined with the value for $\Delta H°$ to yield the value of 5.1(2) J K^{-1} mol^{-1} for the standard conformational entropy difference $\Delta S°$. The kinetic data have also been used to calculate the enthalpy and entropy of activation for the interconversion from trans to cis conformer, and were found to be 44.0(14) kJ mol^{-1} and 16(9) J K^{-1} mol^{-1}, respectively. The results are discussed in light of literature data and in light of perturbation Monte Carlo calculations on solvation enthalpy and entropy.

Introduction

In this study we report on infrared spectra of methyl nitrite dissolved in the liquid rare gases argon, krypton, and xenon. The conformational characteristics of this compound have been studied many times, using various techniques. Most of the older vibrational and rotational literature has been previously reviewed.[1,2] Considerable information has also been obtained from NMR spectroscopy,[3−11] and a survey of the recent literature shows that the interest in the physical chemistry of methyl nitrite has not waned.[12−19] These studies prove that in the fluid phases methyl nitrite occurs as a mixture of cis and trans conformers. The thermodynamic parameters $\Delta H°$, $\Delta S°$, and $\Delta G°$ of the conformer equilibrium in the vapor phase and in several solvents have been measured. [1,2,4,13] It is well-known that the vibrational spectroscopic determination of the entropy difference $\Delta S°$ in solution is difficult when the conformers are at equilibrium.[20,21] As a consequence, the literature $\Delta S°$ values obtained with infrared spectroscopy are limited to the vapor phase.[13] They have been measured either directly in that phase or indirectly, using matrix isolation techniques, in which it was assumed that the population ratios observed in the matrixes are determined by temperature of the nozzle through which methyl nitrite vapors were deposited in the matrix.[13] In the present study we explicitly address the infrared spectroscopic determination of the standard entropy difference $\Delta S°$ in solution.

When infrared spectroscopy is used, the ratio of the extinction coefficients of a conformational doublet in the spectrum must be known if $\Delta S°$ is to be calculated.[20] Methods to measure this ratio have been proposed and have been reviewed by A. I. Fishman et al.[22−25] Of the proposed methods, only two turn out to give reliable results. In a first method,[24] the kinetics of the conformer equilibration must be investigated, while in the second method spectral measurements must be performed in two temperature intervals: one in which the equilibration velocity is negligible with respect to the time required to record an infrared spectrum; the other in which the equilibration is virtually instantaneous on the same time scale.[23−25] It has been observed that when conventional infrared spectroscopy is used as a detection technique, the time scale requires that the barrier to interconversion of the conformers must be relatively high.[25] The barrier separating the cis and trans conformers in methyl nitrite falls in this category, its activation enthalpy being 48 kJ mol^{-1} in the vapor phase, as determined by NMR spectroscopy.[6] Using this value, and assuming that the preexponential factor A of the Arrhenius equation falls in the range between 10^{11} and 10^{14} s^{-1}, it is easy to show that at temperatures in the interval between 140 and 180 K relaxation times result that comply with the requirements of the proposed technique. This temperature range is covered by cryospectroscopy, in which liquid rare gases are used as a solvent.[26] In this study we have investigated solutions in liquid argon, krypton, and xenon, and it was found that kinetic measurements could indeed be performed in liquid krypton. These measurements have yielded extinction ratios for two conformational doublets. The conformational entropy derived using them, and using the conformational enthalpy difference $\Delta H°$ measured in the same solvent, agrees with the literature data.[4,13] The kinetic measurements were also used to calculate the enthalpy and entropy of activation. The results of all this will be discussed in the next paragraphs.

Experimental Section

The sample of methyl nitrite was prepared by mixing equivalent amounts of methanol and nitrosyl chloride at temperatures below −20 °C, and was purified using a low-temperature, low-pressure fractionation column. The solvent gases, argon, krypton, and xenon, were obtained from L'Air Liquide and had stated purities of 99.9999, 99.998, and 99.995%, respectively.

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All infrared spectra were recorded using a Bruker IFS 66v spectrometer equipped with a globar source, a Ge/KBr beam splitter and a liquid N_2-cooled broad-band MCT detector. The interferograms, recorded at a resolution of 0.5 cm^{-1}, were averaged over 200 scans, Blackmann-Harris apodized, and Fourier transformed using a zero filling factor of 8.

Infrared spectra of solutions in liquid rare gases were recorded in two different cells. The kinetic measurements were made between 150 and 160 K. At these temperatures the vapor pressure of liquid krypton (LKr) varies between, approximately, 6 and 10 bar. Therefore, these measurements were made in a standard 4 cm brass cell that is designed for use at pressures up to 15 bar.[26] The solutions in liquid argon and liquid xenon were made in the same cell. The determination of the standard enthalpy difference $\Delta H°$ in LKr requires measurements at temperatures above 160 K. The upper limit used in LKr was 205 K, close to the critical point (209.39 K) of LKr, at which the saturated vapor pressure reaches 48 bar. It follows that these measurements had to be made in a high-pressure stainless steel cell. This cell had a path length of 7 cm. Both cells had wedged silicon windows. The cells were filled and evacuated using a pressure manifold using procedures described before.[27]

Solvation Gibbs energies were obtained from Monte Carlo perturbation calculations, using a modified version of BOSS 4.1.[28] All simulations were run in the NPT ensemble, using standard procedures including a cubic box and periodic boundary conditions. The system consisted of one solute molecule surrounded by 256 solvent atoms. For all simulations, the Metropolis sampling was augmented by preferential sampling[29] in which the probability of attempting to move a solvent atoms was made proportional to $1/(r^2 + c)$, where r is the solute−solvent distance. The constant c was fixed at 250 Å^2, which causes the solvent atoms nearest the solute to be moved twice as often as the most distant solvent atoms. An attempt to move the solute molecule was made on every 50th configuration, and a change in volume was tried on every 600th configuration. The ranges for the attempted moves were the same in each solvent, and provided a ∼40% acceptance probability for new configurations.

The path from $\lambda = 0$ (pure krypton) to $\lambda = 1$ (a solution with one solute molecule) was completed in 32 steps, each step corresponding roughly to $\Delta\lambda = 0.0312$. Advantage was taken of double-wide sampling[30] that permits obtaining two Gibbs energy changes at each step, i.e., that between the reference system at which the simulation is performed ($\lambda = \lambda_0$) and two perturbed systems with $\lambda = \lambda_0 \pm \Delta\lambda$. Each step consisted of an equilibrition phase of 10.0×10^6 configurations, followed by a production phase of 30.0×10^6 configurations. The Gibbs energy changes between perturbed and reference systems were always small enough ($\approx kT$) to guarantee reliable results by the statistical perturbation theory. A single determination of $\Delta_{sol}G$, involving all necessary steps from $\lambda = 0$ to $\lambda = 1$, took approximately 22 h on a dual processor 800 MHz Pentium III computer running Redhat Linux 6.2.

To extract the enthalpy of solvation $\Delta_{sol}H$ and the entropy of solvation $\Delta_{sol}S$ in LKr, the free energy of solvation $\Delta_{sol}G$ was calculated at 12 different temperatures between 124 and 179 K, at a pressure of 26.4 bar, i.e., the vapor pressure of LKr at 179 K.[31]

Results

Preparation of Nonequilibrium Solutions. For the cis/trans conformer equilibrium of methyl nitrite Van't Hoff's isochore can be written using Beer's law as:

$$\Delta S° = R\left(\ln \frac{I_{trans}}{I_{cis}} + \frac{\Delta H°}{RT} - \ln \frac{\epsilon_{trans}}{\epsilon_{cis}}\right) \tag{1}$$

where $\Delta S°$ and $\Delta H°$ are the standard entropy and enthalpy differences between the conformers, I_{cis} and I_{trans} are the band areas of a cis and a trans band in the infrared spectrum, respectively, and ϵ_{cis} and ϵ_{trans} are the corresponding extinction coefficients. From this equation it is clear that the calculation of $\Delta S°$ requires the value of $\epsilon_{trans}/\epsilon_{cis}$. Here we follow the method devised by A. I. Fishman et al.,[22] in which the ratio is derived from kinetic measurements, i.e., from measurements in which the equilibration of a nonequilibrium distribution of the conformers is followed as a function of time. These authors propose to prepare a nonequilibrium solution in the following way. In the first step, the compound is crystallized on a metal mesh. In general, the crystallization ensures that only a single conformer is present in the solid. The metal mesh is subsequently immersed in the solvent, typically liquid propane, cooled to a temperature at which the rate of interconversion of the conformers is negligible. The latter condition ensures that at the outset the solution contains only the conformer which was present in the solid. The solution is then warmed to the temperature at which the equilibration can be followed spectroscopically. Besides involving complex manipulations in a cryogenic environment, this method is not indicated for methyl nitrite, because crystallization tends to produce an uncontrollable mixture of both conformers. Therefore, we have adopted a simpler procedure, in which room-temperature vapors of the compound are rapidly frozen into the observation cell, which was cooled to a temperature well below the freezing point of methyl nitrite. The experience is that in the resulting amorphous solid the relative conformer population is close to the room temperature vapor phase equilibrium distribution, which can be anticipated to be far from the low-temperature equilibrium distribution in solution. After the compound is frozen in, the solvent is condensed into the cell, at the same low temperatures, allowing the compound to be dissolved. Finally, as in Fishman's procedure, the cell is warmed to a temperature at which the equilibration can be followed spectroscopically.

Kinetic Measurements. The possibility of following the equilibration was studied in three solvents, argon, krypton, and xenon. In each solvent, solutions were prepared containing approximately 1×10^{-4} mole fraction of methyl nitrite, and the solutions were studied in a standard 4 cm brass cell, in a temperature interval limited on the high-frequency side by the temperature at which the vapor pressure reached 15 bar, the upper limit for this type of cell. In this way, the available temperatures for the different solvents overlap, so that the equilibration was studied in the continuous interval between 90 and 230 K. For each solvent, the spectrum was measured at several temperatures. For each spectrum, band areas were determined for the ν_3 (1670 (trans)/1615 (cis) cm^{-1}) and ν_8 (838 (cis)/807 (trans) cm^{-1})[1] conformer doublets, using Voigt profile least-squares band fitting of the experimental contours. For the complete temperature interval in LAr, between 90 and 120 K, the ratios of the band areas of the doublets remained constant, signaling that no population relaxation occurred. For the solutions in LXe, studied between 165 and 230 K, the changes in the ratios were consistent with a near-instantaneous equilibration of the conformer distribution. At temperatures below 150 K in LKr, no changes in the ratios were observed. Just above 150 K irreversible changes started to occur, indicating that relaxation took place, while at temperatures above 160 K, the equilibration was found to be fast on the time scale of the spectroscopic experiment. These observations are in agreement

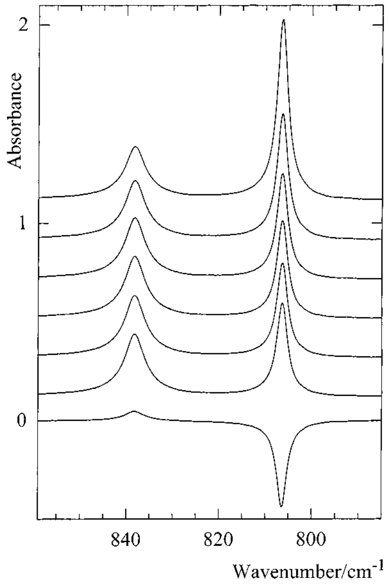

Figure 1. The ν_8 region of the infrared spectra of methyl nitrite disolved in LKr, at 152 K, during an equilibration experiment. For the top six traces, time increases from top to bottom, the top trace giving the first recorded spectrum, the sixth trace giving the last. The spectra have been shifted vertically for clarity. The lower trace is the difference between the last and the first spectra.

with the anticipated temperature interval. Starting from a fresh solution for each temperature, the equilibration was studied at five different temperatures between 149.5 and 158.4 K, by recording spectra with a time interval varying between 2 (higher temperatures) and 10 min (lower temperatures).

As an example, in Figure 1 a few of the spectra recorded during an experiment at 152 K are shown as a function of time, the series starting with the top spectrum. The conformational relaxation is particularly clear from the lower trace, which gives the difference between the last and the first spectra of the series. It can be seen that during the experiment the cis band at 838 cm^{-1} increases in intensity, while the trans band at 807 cm^{-1} decreases, it being clear that the increase of the cis band intensity is much smaller than the decrease of the intensity of the trans band. Because the measurements were made at constant total concentration, this shows there is a significant difference between the extinction coefficients of the bands. Figure 2 reports some of the results obtained for the band areas. The upper panel gives the time evolution of the trans component of ν_3 at two different temperatures, and the lower panel gives the behavior of the corresponding cis band area. The rapid decrease of the relaxation time with increasing temperature is obvious.

Determination of Extinction Ratios. For isothermal measurements at a constant total concentration C, the following relation between the band areas is easily derived:[22]

$$I_{\mathrm{trans}} = -\left(\frac{\epsilon_{\mathrm{trans}}}{\epsilon_{\mathrm{cis}}}\right) I_{\mathrm{cis}} + \epsilon_{\mathrm{trans}} l C \qquad (2)$$

in which l is the path length of the cell. Because of the dilution of the solutions studied, it is unlikely that the relaxation affects the extinction coefficients. Hence, this relation predicts that I_{cis} varies linearly with I_{trans}, with the slope given by the ratio of the extinction coefficients. The linearity is illustrated in Figure 3 for the ν_8 doublet, using the spectra recorded at two different temperatures. A linear regression was performed using the data obtained for ν_3 and ν_8 at the five different temperatures, and the average slopes $\epsilon_{\mathrm{trans}}/\epsilon_{\mathrm{cis}}$ were found to be 1.2(2) for the ν_3 doublet and 4.8(8) for the ν_8 doublet.

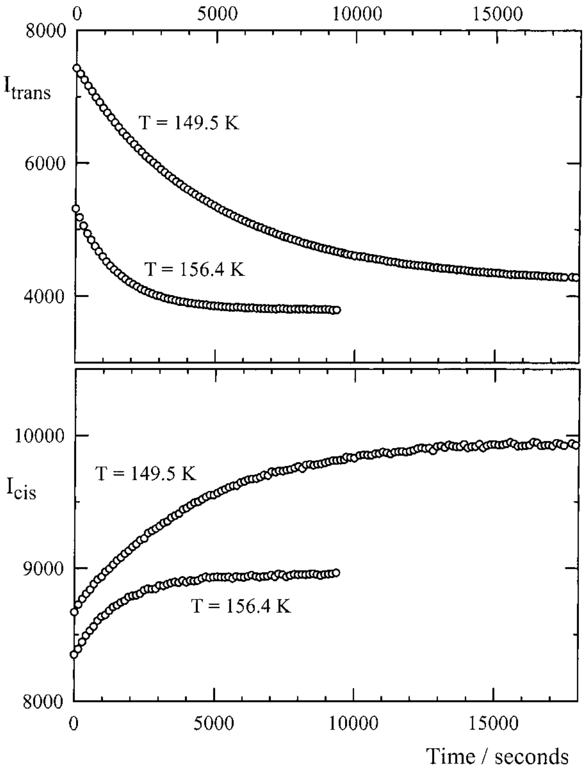

Figure 2. Time evolution of the band areas of the ν_3 doublet of methyl nitrite during equilibration experiments. The upper panel gives the behavior of the 1670 cm^{-1} trans band during experiments performed at the indicated temperatures; the lower panel gives the evolution of the cis band.

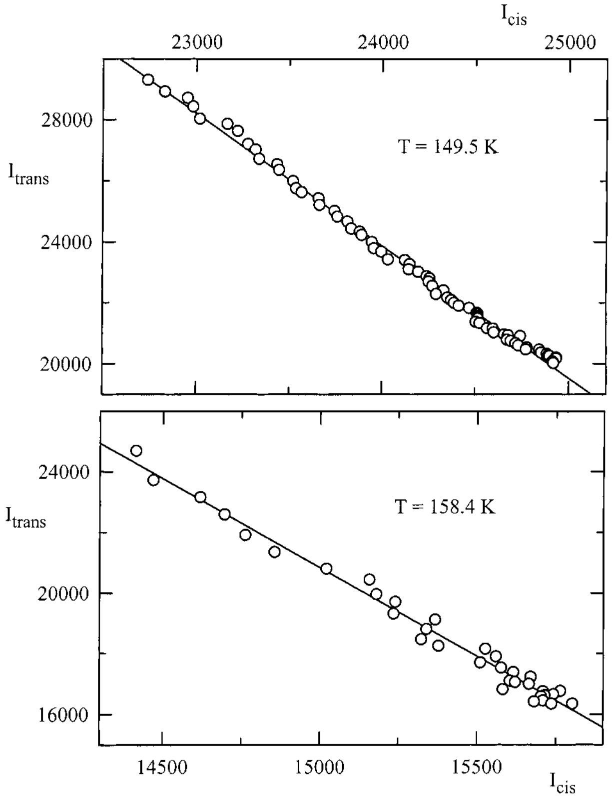

Figure 3. Plots of the band area of the ν_8 trans band of methyl nitrite versus that of the cis band during equilibration experiments performed at the indicated temperatures.

Enthalpy Difference. The calculation of $\Delta S°$ further requires a value for the standard enthalpy difference $\Delta H°$. This quantity

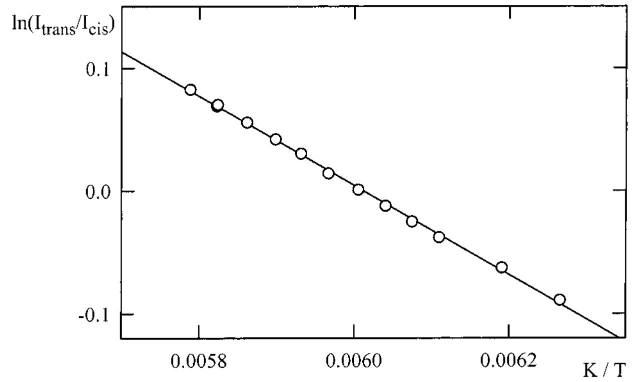

Figure 4. Van't Hoff plot for the determination of the enthalpy difference $\Delta H°$ between the trans and cis conformers of methyl nitrite disolved in liquid krypton. The band areas were taken from the ν_8 conformational doublet.

has been determined in other environments,[13] but to avoid eventual solvent effects on it, we have determined its value in the same solvent liquid krypton as used to measure the extinction ratios. To this end, measurements were performed between 165 and 205 K, in the temperature interval in which the cis/trans interconversion is fast on the time scale of the infrared experiment. As said before, these measurements had to be performed in a high-pressure stainless steel cell. In contrast with measurements in the brass cell, in contact with stainless steel a slow decomposition of the compound was observed. The decomposition products gave rise to weak bands in the 1600−1850 cm^{-1} range. Their frequencies suggest they are due to N_2O_3 and N_2O_4.[32] The slow decrease of the total concentration is of no consequence for a Van't Hoff analysis of the conformational doublet, but particularly the 1631 cm^{-1} N_2O_3 band was found to cause problems in the band fitting of the ν_3 doublet, so that the resulting band areas were judged to be insufficiently reliable. The identified impurities cause no bands in the 850−800 cm^{-1} region, and, consistent with this, no impurity bands were detected in this region. Therefore, $\Delta H°$ was determined using the ν_8 doublet. The Van't Hoff graph resulting from plotting the logarithm of the band area ratio I_{trans}/I_{cis} against $1/T$ is shown in Figure 4. The value of $\Delta H°$ obtained from the slope of the regression line equals 3.02(9) kJ mol^{-1}, the cis conformer being more stable.

Entropy Difference. It is easily shown that, as a variation of eq 1, the intercept b of the regression line of the Van't Hoff plot equals $\Delta S°/R - \ln(\epsilon_{trans}/\epsilon_{cis})$. In principle, extinction coefficient ratios may depend on the temperature.[20,21] The experimental values of $\epsilon_{trans}/\epsilon_{cis}$ have been determined in the temperature interval between 150 and 158 K, with an average of 154 K, a value slightly lower than the average temperature of the interval used for the measurement of $\Delta H°$, 185 K. The intercept is valid at the latter temperature, and in order to obtain the correct value for $\Delta S°$, the value of $\ln(\epsilon_{trans}/\epsilon_{cis})$ at this temperature should be used. Linear regression of the $\epsilon_{trans}/\epsilon_{cis}$ values obtained at the five temperatures of the kinetic measurements, using temperature as the abscissa, results in a small nonzero, positive slope. Its uncertainty, however, equals twice its value, so that the result is not statistically meaningfull. Therefore, for the calculation of $\Delta S°$, no temperature correction was applied to $\ln(\epsilon_{trans}/\epsilon_{cis})$.

The intercept b of the regression line in Figure 4 is calculated to be 2.18(4), and using the value of $\epsilon_{trans}/\epsilon_{cis}$ derived above, the standard entropy difference $\Delta S°$ is found to be 5.1(2) J K^{-1} mol^{-1}.

A second method to determine $\Delta S°$ has been proposed by Fishman et al.[23−25] In this method, spectra must be recorded from a solution with constant total concentration, in two different intervals of temperature. In the first interval the rate of interconversion of the conformers must be negligible, so that the temperature dependence of the band area reflects the temperature dependence of the extinction coefficient of that band. In the cases discussed,[23−25] this relation is linear and the regression is used to determine the extrapolated band area at a temperature T in the second temperature interval, in which the conformers are in equilibrium. Combined with the observed band area at that temperature T, the value of $\Delta S°$ can be calculated, as shown by the relations derived by Fishman et al.[23] In principle, our measurements on methyl nitrite in LKr are amenable to such an analysis because, as was said above, at temperatures below 150 K the rate of interconversion rapidly becomes negligibly small. The assumption of constant molar concentration across the two temperature ranges will not strictly hold for solution in LKr, in view of the significant thermal expansion of the solvent, but the equations can be modified to take this into account. However, the analysis failed because of the slow decomposition of methyl nitrite in the high-pressure stainless steel cell, so that the assumption of a constant total concentration was not justified. Therefore, this analysis could not be further pursued. It is interesting to note that a slight decomposition of the compound when in contact with stainless steel was observed before.[13]

Transition State Parameters. The kinetic data discussed above have also been used to derive the thermodynamic characteristics of the transition state. In the first step, the kinetic data were least-squares fitted to a relation of the form

$$I_a(t) = I_a(\mathrm{eq}) + \alpha \exp(-\beta t) \qquad (3)$$

in which $I_a(t)$ is the area of a band of conformer "a" at time t, $I_a(\mathrm{eq})$ is the corresponding band area at equilibrium, and α and β are constants.

Because the enthalpy difference between the cis and trans conformers is relatively small, at temperatures where the interconversion from the less stable trans to the cis conformer can be followed spectroscopically, the interconversion in the opposite direction, from cis to trans, cannot be neglected. In such a case, the kinetic experiments are governed by a relation of the form given in eq 3, in which β has the value[33]

$$\beta = k_c(T) + k_t(T) \qquad (4)$$

where k_c and k_t are the interconversion rates, at temperature T, from cis to trans, and from trans to cis, respectively.

Transition state theory allows the Arrhenius equation for a rate constant $k_i(T)$ to be written as[34]

$$k_i(T) = \frac{k_B T}{h} \exp(\Delta^{\dagger} S_i°/R) \exp(-\Delta^{\dagger} H_i°/RT) \qquad (5)$$

in which $\Delta^{\dagger} H_i°$ is the standard enthalpy of activation and $\Delta^{\dagger} S_i°$ is the standard entropy of activation, for conformer i. Using this expression, the ratio $k_c(T)/k_t(T)$ of the interconversion rates is obtained as

$$\frac{k_c(T)}{k_t(T)} = \exp[(\Delta^{\dagger} S_c° - \Delta^{\dagger} S_t°)/R] \exp[-(\Delta^{\dagger} H_c° - \Delta^{\dagger} H_t°)/RT] \qquad (6)$$

Because both interconversions proceed via the same activated complex, the difference in standard activation entropies in eq 6

TABLE 1: Trans→Cis Transition Rates k_t for Methyl Nitrite Disolved in Liquid Krypton

	$k_t \times 10^4$/s^{-1}	
T/K	ν_3	ν_8
149.5	1.84(4)	1.96(4)
151.9	3.31(8)	3.42(8)
154.2	5.35(13)	5.88(23)
156.4	9.09(24)	9.54(23)
158.4	14.83(38)	15.02(38)

equals the standard entropy difference between the conformers:

$$\Delta^{\dagger}S_c^{\circ} - \Delta^{\dagger}S_t^{\circ} = \Delta S^{\circ} \tag{7}$$

Similarly, the difference between the standard activation enthalpies equals the standard enthalpy difference between the conformers:

$$\Delta^{\dagger}H_c^{\circ} - \Delta^{\dagger}H_t^{\circ} = \Delta H^{\circ} \tag{8}$$

Therefore, eq 6 can be written as

$$\frac{k_c(T)}{k_t(T)} = \exp\,(\Delta S^{\circ}/R)\,\exp(-\Delta H^{\circ}/RT) = \exp(-\Delta G^{\circ}/RT) = p \tag{9}$$

The quantities ΔS° and ΔH° have been obtained above, so that the ratio p can be calculated. With this, eq 3 can be written for the behavior of a trans band as

$$I_t(t) = I_t(\mathrm{eq}) + \alpha\,\exp[-k_t(1+p)t] \tag{10}$$

Thus, the exponential regression curves through the experimental kinetic points describing the time evolution of the band area of a trans band can be used to obtain k_t at different temperatures. From this, $\Delta^{\dagger}S_t^{\circ}$ and $\Delta^{\dagger}H_t^{\circ}$ can be calculated using eq 5.

The values of k_t have been derived starting from band areas of the trans component of ν_3 and ν_8. Both sets have been collected in Table 1. It can be seen that the agreement between the sets is good. The Arrhenius plot of the combined $\ln[(hk_t/(k_BT)]$ versus $1/T$ is given in Figure 5. The linear regression line yields a value of 44.0(14) kJ mol^{-1} for $\Delta^{\dagger}H_t^{\circ}$ and of −16(9) J K^{-1} mol^{-1} for $\Delta^{\dagger}S_t^{\circ}$.

Discussion

Numerical values obtained in this study for extinction coefficient ratios, standard enthalpy and entropy difference between the conformers, and activation enthalpy and entropy, have been collected in Table 2, in which also the relevant literature data on these quantities are given.

Extinction Coefficient Ratios. Extinction coefficient ratios $\epsilon_{trans}/\epsilon_{cis}$ for ν_3 and ν_8 have been reported by Bodenbinder et al.,[13] as measured in argon matrixes. The values obtained are 1.04 for ν_3 and 3.3 for ν_8, which have to be compared with our values of 1.2(2) and 4.8(8), respectively. The environments in which the two sets have been obtained do not differ greatly, so the results should be similar. Yet, for ν_8 the values differ considerably. A critical evaluation of the method employed by Bodenbinder et al.[13] suggests that their ratios may be less accurate for several reasons. In the first place there is the total concentration of CH_3ONO in the matrix which must be known to derive the ratio. It was measured by preparing matrixes from gas phase mixtures of CH_3ONO and SiF_4 with known relative concentrations and using the SiF_4 bands as internal standards. Because SiF_4 is much more volatile than CH_3ONO, it cannot be excluded that SiF_4 is deposited less completely, so that the concentration ratio is affected by the deposition process. Second, some decomposition of methyl nitrite was observed,[13] which, as discussed above, may be due to the contact of CH_3ONO with the stainless steel nozzle system used to deposit the matrixes: also this affects the SiF_4/CH_3ONO concentration ratio. Finally, the reported resolution[13] used to record the spectra is 1 cm^{-1}, which may be insufficient to produce reliable band areas for the very sharp bands that appear in the matrix spectra. These factors do not influence our measurements, which, therefore, we believe to be more accurate.

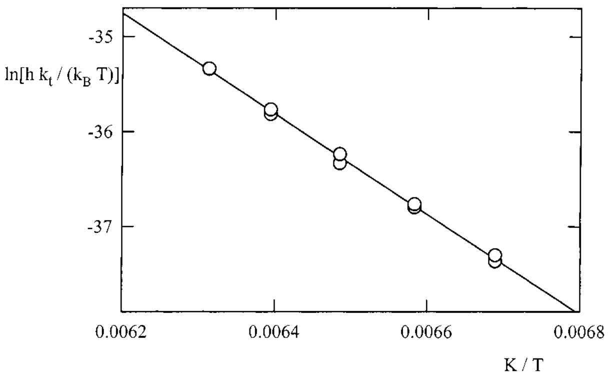

Figure 5. Arrhenius plot for the determination of the enthalpy and entropy of activation of the trans conformer of methyl nitrite.

It is the general experience with cryosolutions that relative infrared intensities are approximately preserved at the gas-to-liquid transition.[35] Assuming this is the case for methyl nitrite, our experimental extinction ratios can be compared with the ratios of ab initio infrared intensities calculated for a single molecule, i.e., for the dilute gas phase. Although the absolute values of theoretical intensities do not always have the desired accuracy, it appears justified to assume that the ratio of intensities of the same vibrational mode in two conformers of the same compound is predicted with acceptable accuracy. Ab initio intensities for methyl nitrite, at the MP2 level, have been published by Da Silva et al.[14] for basis sets varying from 6-31G to 6-311++G**. The values obtained from the different basis sets are rather similar and give an average trans/cis intensity ratio of 1.3 for ν_3 and 4.3 for ν_8. In this study we have expanded the available data to include DFT results, calculated using

TABLE 2: Trans/Cis Extinction Ratios ($\epsilon_{trans}/\epsilon_{cis}$) for ν_3 and ν_8, Standard Enthalpy Difference, ΔH° (in kJ mol^{-1}), Standard Entropy Difference, ΔS° (in J K^{-1} mol^{-1}), Activation Enthalpy $\Delta^{\dagger}H_t^{\circ}$ (in kJ mol^{-1}), and Activation Entropy, $\Delta^{\dagger}S_t^{\circ}$ (in J K^{-1} mol^{-1}), for Methyl Nitrite

environment	$\epsilon_{trans}/\epsilon_{cis}(\nu_3)$	$\epsilon_{trans}/\epsilon_{cis}(\nu_8)$	ΔH°	ΔS°	$\Delta^{\dagger}H_t^{\circ}$	$\Delta^{\dagger}S_t^{\circ}$
liquid krypton[a]	1.2(2)	4.8(8)	3.02(9)	5.1(2)	44.0(14)	−16(9)
vapor phase	1.02[13]		3.5(2)[13]	8.5(10)[13]	47.9(17)[6]	−6.0(17)[6]
neat liquid			3.13(4)[1]		51.0(9)[6]	9.1(10)[6]
1% in CS_2					50.0(11)[6]	5.8(12)[6]
Ar matrix	1.04[13]	3.3[13]				

[a] This study.

Gaussian 98,[36] at the B3LYP level, using the basis sets of Da Silva et al.,[14] expanded with the basis sets aug-cc-PVDZ and aug-cc-PVTZ. For ν_3 the calculated ratio ranges from 1.34 to 1.54, with an average of 1.4, while for ν_8 the ratio varies between 4.99 and 5.64, with an average of 5.4. For ν_3, our experimental value of 1.2(1) is closer to the MP2 result, while for ν_8 our value falls between the MP2 and DFT values, albeit somewhat closer to the average MP2 value. Altogether it is clear that the predicted ratios confirm the experimental trends, i.e., that the ratio for ν_3 is close to 1, while it is significantly higher for ν_8. There is little doubt that this is connected with the nature of the modes involved, as reflected from their potential energy distribtutions:[37,1,14] for ν_3 the latter are nearly identical in cis and trans, while for ν_8 the contributions of the ν(N−O), ν(C−O), ν(N═O), and $\gamma(CH_3)$ internal coordinates in cis differ greatly from those in the trans conformer. The potential energy distributions strongly differ, and it is not surprising that the trans extinction coefficient for ν_8 differs markedly from that for the cis conformer.

Entropy Difference. The entropy difference Δ*S*° between the conformers has been investigated using NMR spectroscopy[4] and infrared spectroscopy,[13] and has been calculated using statistical thermodynamics.[13] The values obtained refer either to the vapor phase or to solutions. For the vapor phase an average experimental value of 8.5(10) J K^{-1} mol^{-1} was derived,[13] the individual values ranging from 6.9(35) to 9.7(10) J K^{-1} mol^{-1}, while values in solution range from 7.4(10) (1% in CS_2) to 8.3(10) J K^{-1} mol^{-1} (1% in acetone-d_6).[4]

The important entropy difference between trans and cis conformers has been attribtuted to be mainly due to the methyl torsion, which is quasi-free in the trans, but is hindered by a barrier of some 9.5 kJ mol^{-1} in the cis conformer.[13]

The above data suggest that in solution the Δ*S*° is somewhat smaller than in the vapor phase. This aspect was more closely investigated by calculating the Gibbs energy of solvation, $\Delta_{sol}G$, for the conformers in LKr, using Monte Carlo Perturbation calculations.[38−41] The calculations were made with the BOSS 4.1 program.[28] The solvation enthalpies and entropies were extracted from the Gibbs energies using a finite difference method similar to the one decribed by Levy et al.[42,43]

To accurately describe the solvation of polar species in liquefied rare gases, solute−solvent polarization effects must be explicitly accounted for. Therefore, the intermolecular interactions were modeled by a combination of Lennard-Jones and polarization terms. A Lennard-Jones function was used for each pair of atoms. The parameters of these functions were taken from the OPLS all-atom potential functions.[44] The standard BOSS 4.1 program does not allow to take into account polarization contributions. Therefore, additional code was added to the program, in which the polarization energy between the solute and a nearby rare gas atom is calculated using a noniterative first-order approximation:[45,46]

$$E_{pol} = -\frac{1}{2}\vec{\mu}_{ind}\cdot\vec{E} = -\frac{1}{2}\alpha_{solvent}(\vec{E}\cdot\vec{E}) \qquad (11)$$

where $\alpha_{solvent}$ refers to the polarizability of the rare gas studied,[34] and $\vec{E}$ is the electric field generated by the solute. This field was calculated from a charge model of the molecule. The Coulomb charges, located on the nuclei, were optimized using Gaussian 98[36] so as to reproduce the dipole moment and the electric field around the molecule. The calculations were made at the B3LYP/6-311++G(d,p) level.

The calculated solvation entropies $\Delta_{sol}S$ and enthalpies $\Delta_{sol}H$ are collected in Table 3. It can be seen that the introduction of methyl nitrite into LKr reduces the entropy of the combined system by more than 80 J K^{-1} mol^{-1}, with the decrease for the trans conformer slightly bigger than that for the cis conformer. The difference may be attributed to the extended conformation of the trans and to its slightly higher dipole moment,[47] both factors favoring a slightly stronger solvation than for the cis conformer. The net solvation influence, ΔΔ*S*°, on Δ*S*° is a decrease of the vapor phase value by 1.9(16) J K^{-1} mol^{-1}. It can be seen in Table 3 that the solvation entropies for the individual conformers were obtained with small relative uncertainties. However, because the two contributions nearly cancel, a considerable uncertainty on ΔΔ*S*° results.

TABLE 3: Solvation Entropies and Enthalpies for the Conformers of Methyl Nitrite in Liquid Krypton, and Solvation Influences on Standard Entropy and Enthalpy Differences

conformer	$\Delta_{sol}S$/J K^{-1} mol^{-1}	$\Delta_{sol}H$/kJ mol^{-1}
trans	−84.5(11)	−30.23(24)
cis	−82.6(16)	−29.82(16)
ΔΔ*S*°	−1.9(16)	
ΔΔ*H*°		−0.4(3)

Starting from the average vapor phase Δ*S*° of Bodenbinder et al.,[13] 8.5(10) J K^{-1} mol^{-1}, and applying the Monte Carlo correction, a value of 6.6(19) J K^{-1} mol^{-1} for Δ*S*° in LKr results. The experimental value obtained above is 5.1(2) J K^{-1} mol^{-1}. Despite the limited temperature interval used to obtain the Van't Hoff regression line, the uncertainty on this value is relatively small, which is a consequence of the high linearity of the experimental points in the Van't Hoff plot. The experimental Δ*S*° value is somewhat smaller than the predicted value, but the uncertainty limits of both values overlap considerably, which means that the agreement may be considered to be acceptable.

Enthalpy Difference. Table 3 also shows that the solvation enthalpies for the conformers are nearly equal, so that the solvent influence ΔΔ*H*° on Δ*H*° is limited to a decrease by 0.4(3) kJ mol^{-1}. This near cancellation results, just as for the entropies, in an important relative uncertainty.

Combining their own results with the available literature data, Bodenbinder et al.[13] arrive at an average vapor phase Δ*H*° of 3.5(2) kJ mol^{-1}. Applying the above solvent correction, the Δ*H*° in LKr is predicted to be 3.1(4) kJ mol^{-1}. Our experimental value of 3.02(9) kJ mol^{-1} is in excellent agreement with this prediction. The lowering of Δ*H*° is in line with the NMR results of Chauvel et al.,[4] who report a vapor phase Δ*H*° of 4.17(21) kJ mol^{-1}, and values of 3.42(1), 3.6(2), 3.4(2), and 3.5(3) kJ mol^{-1} for the neat liquid and for solutions in acetone-d_6, carbon disulfide, and *n*-pentane, respectively, the value for the neat liquid being corroborated by the Raman result of 3.14(4) kJ mol^{-1}.[1]

Transition State Parameters. Finally, there remains the comparison of the transition state parameters $\Delta^{\dagger}H_t°$ and $\Delta^{\dagger}S_t°$ that have been obtained in this study with the results from NMR spectroscopy.[6] The data have been collected in Table 2. In the NMR study, $\Delta^{\dagger}H_t°$ is found to be 47.9(17) kJ mol^{-1} in the vapor phase, and slightly higher in the neat liquid, 51.0(9) kJ mol^{-1}, and in solution in carbon disulfide, 50.0(11) kJ mol^{-1}. The higher values in the liquid phase are explained[6] by the larger molar volume of the transition state, due to the free internal rotation around the N−O bond. This model suggests that in LKr the $\Delta^{\dagger}H_t°$ should also be higher than in the vapor phase. However, the $\Delta^{\dagger}H_t°$ in LKr is smaller, by 3.9 kJ mol^{-1}. It follows that the vapor phase value is too high, that the value for LKr is too low, or both. The $\Delta^{\dagger}S_t°$ value for LKr, −16(9)

J K^{-1} mol^{-1}, has the same sign as for the vapor phase, $-6(2)$ J K^{-1} mol^{-1}, but the reported values in the liquid phases[6] have the opposite sign. This suggests that our $\Delta^{\dagger}S_t^{\circ}$ may have the wrong sign. A higher slope of the Arrhenius plot resulting in a higher value for $\Delta^{\dagger}S_t^{\circ}$, an erroneous sign of $\Delta^{\dagger}S_t^{\circ}$ might be due to the fact that the LKr value for $\Delta^{\dagger}H_t^{\circ}$ is somewhat low. That, on the other hand, the vapor phase NMR value probably is too high can be seen as follows. From their vapor phase results, Chauvel et al.[6] derive the potential governing the internal rotation around the N−O bond. The trans→cis barrier in their potential equals 4141 cm^{-1}, and the torsional fundamentals in this potential are calculated at 296 cm^{-1} for the cis conformer and 229 cm^{-1} for the trans conformer.[6] These fundamentals have since then been observed in the vapor phase far-infrared spectra, at 247 and 213 cm^{-1}, respectively.[2] The trans→cis barrier derived from these frequencies is 3507 cm^{-1}, lower by 634 cm^{-1}, or 7.6 kJ mol^{-1}, than the NMR value. This means that the vapor phase NMR value for $\Delta^{\dagger}H_t^{\circ}$ could be too high by the same amount. Correcting the vapor phase value with this results in a value of 40.3 kJ mol^{-1}, which is 3.7 kJ mol^{-1} lower than the LKr value. This correction brings the vapor phase value in line with the expected increase of $\Delta^{\dagger}H_t^{\circ}$ at the vapor−solution transition.

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