has little importance in curve fitting at our molalities, but the first two affect the calculated activity coefficients in sufficiently orthogonal ways that they can be adjusted without a formal fitting routine. One of the features of Pitzer's equations is that they can be used to calculate activity coefficients for mixtures from the parameters derived for the components. In our case, we will do the reverse since our measurements are for dilute solutions of NaHSe in NaOH. The equation for mixtures of two 1-1 electrolytes is particularly simple and is given in Pitzer's review.[3]

A good fit to our activity coefficients for NaHSe in NaOH is obtained by lowering $\beta^{(0)}$ for NaHSe below that of NaOH and keeping the others the same. We obtain a good fit by setting $\beta^{(0)}_{\mathrm{NaHSe}} = 0.040$, which is below the 0.0864 value of NaOH. The Pitzer equations can then be used to predict the directly measurable activity coefficient of essentially pure NaHSe solutions, but containing a very small amount of NaOH to prevent hydrolysis. They indicate that the mean activity coefficient should pass through a minimum near 2 *m* with a value of 0.58. If we compare the Pitzer parameters of NaF, NaCl, and NaBr, we find that the $\beta^{(0)}$ parameters uniformly increase in going from NaF to NaBr. However, K^+ and Rb^+ do show a decrease in going from F^- to Cl^- with correspondingly lower activity coefficients. No data are available for protonated ions similar to OH^- and HSe^-.

Conclusions

The ultraviolet spectra of HSe^- and Se^{2-} can be used to determine the second dissociation constant for H_2Se, if their interesting spectral shifts with ionic strength are taken into account. The extrapolation of the equilibrium constants measured at ionic strengths well above 0.1 to 0 ionic strength requires some knowledge of the activity coefficients of HSe^- and Se^{2-} in our NaOH solutions, and we think that the solubilities of two hydrates of Na_2Se have provided us with that information. Since the previous work by Wood on H_2Se had guarded against air oxidation, our value for K_2 is within his large experimental error. As a result, there is no large jump in the literature values of K_2 for H_2Se as has been the case for H_2S.

Acknowledgment. We thank Professors R. E. Connick and K. S. Pitzer for helpful discussions. The work was partially supported by the Committee on Research of the Berkeley campus.

Registry No. H_2Se, 7783-07-5; Se^{2-}, 22541-48-6; NaHSe, 12195-50-5.

Vibrational Photochemistry of Porphine Imbedded in a *n*-Hexane-d_{14} Shpol'skii Matrix

Thomas J. Butenhoff, Roy S. Chuck,[†] Hans-Heinrich Limbach,[‡] and C. Bradley Moore*

Department of Chemistry, University of California, Berkeley, and Materials and Chemical Sciences Division of the Lawrence Berkeley Laboratory, Berkeley, California 94720 (Received: January 16, 1990)

The near-infrared-induced tautomerization of free-base porphine incorporated in a *n*-hexane-d_{14} matrix is reported. Porphine occupies two sites in a *n*-hexane-d_{14} matrix as opposed to one site in a *n*-hexane matrix. Two spectroscopically distinct tautomers, differing by a 90° rotation of the NH bond axes within the molecular plane, exist for each site. Nernst glower irradiation on the NH stretch fundamental does not induce tautomerization, but irradiation in the regions $4000 < \nu < 5100$ cm^{-1} and $5630 < \nu < 7700$ cm^{-1} does induce tautomerization. Narrow-band (8 cm^{-1} fwhm) laser irradiation studies in the NH symmetric plus antisymmetric stretch combination band region ($6300 < \nu < 6600$ cm^{-1}) show that the near-infrared-induced tautomerization occurs at select wavelengths. Tautomer conversion in absence of site conversion is strong evidence that the observed photochemistry is due to absorption of light by porphine and not by hexane. The estimated quantum yield is roughly 5×10^{-4} for 6530-cm^{-1} irradiation; this is 1-3 orders of magnitude larger than the quantum yield expected from RRKM theory.

Introduction

Much effort has been spent in trying to use IR lasers to induce reactions in molecules isolated in cryogenic matrices, and several infrared single-photon reactions have been observed.[1-3] These include interconversion of rotamers such as HONO and CH_2F-CH_2OH, reactions and isomerization of $Fe(CO)_4$, and bimolecular reactions of small organic molecules with F_2. There is hope that selective excitation of fundamental or low overtone vibrations will lead to mode-selective chemical reactions.[1,2] Mode selectivity requires that the pumped mode is strongly coupled to the reaction coordinate; this would allow the reaction to be faster than intramolecular vibrational relaxation (IVR). It is advantageous to excite low vibrational levels to reduce the molecular density of states, anharmonic couplings, and the IVR rate. However, this requires the reaction to have a barrier that is low enough to be accessible by single IR or near-IR photon energies. Isolating the molecule in a cryogenic matrix is a useful method to reduce the thermal energy of the molecule and inhibit the thermal reaction which is competing with the vibrational photochemistry. The weak coupling between the guest and the matrix often allows IVR and reaction of the guest to compete with the vibrational energy transfer from the guest to the matrix.

Here, the initial results of the near-infrared-induced tautomerization of free-base porphine (H_2P) imbedded in a *n*-hexane-d_{14} Shpol'skii matrix[4,5] are reported. Limbach and co-workers[6] have measured the activation energy for tetraphenylporphyrin tautomerization and found it to be 3330 cm^{-1}, which shows that it may be possible to cause porphyrin tautomerization reactions by excitation of one or two quanta of the N-H stretch. One may speculate that the N-H stretch is strongly coupled to the reaction coordinate[6-8] (presumably some combination of N-H stretch and bend) which would make porphyrins ideal candidates to exhibit mode-selective chemistry. The initial vibrational photochemistry results reported here prompted the thermal tautomerization studies of ref 9 which showed that the porphine tautomerization proceeds

---

[†] Present address: Department of Molecular and Cell Biology, University of California, Berkeley, CA 94720.

[‡] Institut für Physikalische Chemie der Universität Freiburg i. Br. Albertstrasse 21, D-7800 Freiburg, West Germany.

(1) Frei, H.; Pimentel, G. C. *Annu. Rev. Phys. Chem.* **1985**, *36*, 491.

(2) Cureton, C. G.; Goodall, D. M. *Adv. Infrared Raman Spectrosc.* **1983**, *10*, 307.

(3) Poliakoff, M.; Turner, J. J. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 1980; Vol. 5, pp 175-216.

(4) Shpol'skii, E. V. *Sov. Phys.—Usp.* (*Engl. Transl.*) **1962**, *5*, 522.

(5) Shpol'skii, E. V. *Sov. Phys.—Usp.* (*Engl. Transl.*) **1963**, *6*, 411.

(6) Limbach, H. H.; Hennig, J.; Gerritzen, D.; Rumpel, H. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 229.

(7) Limbach, H. H.; Hennig, J. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 752.

(8) Limbach, H. H.; Hennig, J.; Stulz, J. *J. Chem. Phys.* **1983**, *78*, 5432.

0022-3654/90/2094-7847$02.50/0 © 1990 American Chemical Society

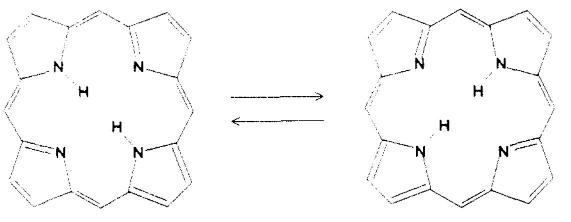

Figure 1. Tautomerization of free-base porphine (H_2P).

via an asynchronous hydrogen migration and the barrier to tautomerization is 4500–5500 cm^{-1}. A better value for the barrier has been obtained by Limbach and co-workers.[10] They have measured tautomerization rates and kinetic isotope effects for porphine in solution. They have simulated their high-temperature and the low-temperature[9] Arrhenius curves with the Bell tunneling model[9,11] and have determined that the barrier to tautomerization in porphine is 4500 cm^{-1}.

At 12 K, porphine occupies two sites in the *n*-hexane-d_{14} matrix. For each site, the porphine has two orientations, or tautomers, which differ by a 90° rotation in the plane of the molecule with respect to the crystal axes;[12] this rotation is equivalent to the exchanging of the two inner hydrogens from one pair of nitrogens to the other (Figure 1). The barrier to the tautomerization is 4500 cm^{-1},[9,10] which is low enough to be energetically accessible by excitation with a single near-infrared photon but high enough to prevent tautomer interconversion at the low temperatures maintained in the matrix.

The two tautomers have different crystal field effects in the matrix. This causes their $S_1 \leftarrow S_0$ absorptions to differ by 100 cm^{-1} while the line widths are only 3 cm^{-1}. The tautomer populations were probed by fluorescence excitation spectroscopy on the $S_1 \leftarrow S_0$ 0–0 band. The tautomers do not thermally interconvert at 12 K, but the tautomer of a given site can be photochemiclly converted to the other tautomer of that site by irradiation on its 0–0 band, and vice versa.

Experimental Section

The porphine samples were made by the method of Voelker et al.:[13] porphine was dissolved at a concentration of $\approx 10^{-6}$ M in *n*-hexane-d_{14} which contained a few percent of ethanol to increase the porphine solubility. The resulting solution was sealed under vacuum in a 4-mm-o.d., 3-mm-i.d., 15-mm-long infrasil tube. The sample tube was fastened in a copper block and mounted in a closed cycle helium refrigerator (Air Products Inc., Model CSA 202). The photolysis experiments were carried out with the sample at 12 K as determined by measuring the emf from a KP vs iron-doped gold (0.7 atomic % doping) thermocouple.

The porphine was probed by fluorescence excitation spectroscopy on the $S_1 \leftarrow S_0$ 0–0 band. The excitation light was provided by an argon ion pumped continuous wave dye laser (Spectra-Physics Model 375, Rhodamine 590 dye, 1-cm^{-1} (fwhm) bandwidth, 30–60 mW). The 2-mm-diameter dye laser beam was incident on the sample without focusing. When probing the sample, the dye laser was attenuated with a 10^{-4} neutral density filter to avoid the photoconversion of the tautomers. A 6-cm-diameter *f*/1.1 lens collected and focused the fluorescence through two Corning RG-645 filters ($\lambda_{pass} > 645$ nm) onto the cooled cathode of an RCA C31034 photomultiplier tube (PMT). The current from the PMT was amplified by a picoammeter and recorded on a strip chart recorder.

Broad-band infrared radiation was provided by the Nernst glower source of a Beckman IR-7 infrared spectrophotometer. Different wavelength irradiation regions were selected with infrared band-pass filters. The average photon flux incident on the sample was estimated by using Planck's blackbody law, the known emissivity of Nernst glowers,[14] measured filter transmittances, and the experimental geometry. The temperature of the operating Nernst glower was measured with an optical pyrometer and was found to be 1430 ± 10 °C. The average flux at the sample per cm^{-1} bandwidth of photolysis light is calculated to be 3×10^{12}, 2×10^{12}, and 6×10^{12} photons cm^{-2} s^{-1} for the photolysis regions of 3250–3680, 4000–5100, and 5600–7700 cm^{-1}, respectively.

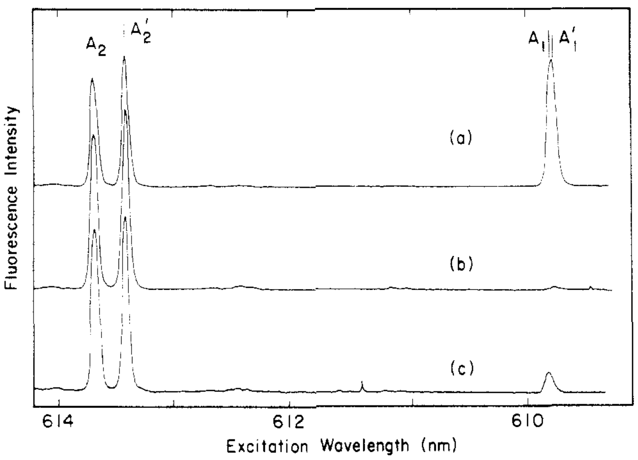

Figure 2. Fluorescence excitation spectrum of H_2P: (a) in *n*-hexane-d_{14}; (b) after burning away most of the A_1 and A_1' tautomers; (c) after 37.2-h Nernst glower irradiation with $5630 < \nu_{phot} < 7700$ cm^{-1}. All spectra are recorded with the sample at 12 K and are not normalized for incident laser power.

A Nd:YAG pumped optical parametric oscillator (OPO) was used for narrow-band infrared photolysis from $6300 < \nu < 6550$ cm^{-1}. The OPO is similar to the design of Byer and Herbst and has been described elsewhere.[15] The OPO was operated at 10 Hz and had a typical signal output power of 3–9 mJ per 10-ns (fwhm) pulse. It was operated without a grating which resulted in an 8-cm^{-1} (fwhm) bandwidth. The unwanted idler beam was removed with a dielectric filter. The 3-mm-diameter beam was directed onto the sample without focusing at right angles to the dye laser beam. Both the probe dye laser beam and the OPO output were plane-polarized with their electric vectors perpendicular to the plane defined by the two laser beams. The average flux on the sample per unit cm^{-1} bandwidth was (3–9 $\times 10^{17}$ photons cm^{-2} s^{-1}. The signal wavelength was measured by reflecting the beam into a calibrated 0.75-m Spex monochromator.

The near-infrared spectra of the samples were measured on a Cary 14 spectrophotometer at room temperature. The short-wavelength tail of the second overtone of the *n*-hexane-d_{14} C–D stretch absorbs in the region investigated by the OPO photolysis. The transmission varied from 68% at 6300 cm^{-1} to 75% at 6550 cm^{-1}.

Results

Figure 2a shows the fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ 0–0 band of H_2P in a *n*-hexane-d_{14} matrix. The site and tautomer labeling convention is that of Völker and van der Waals;[16] capital letters denote the site, and a subscript 1 or 2 denotes the two tautomers. Porphine occupies two sites in a *n*-hexane-d_{14} matrix as opposed to a *n*-hexane matrix, where only one site is occupied. The two sites are labeled A and A′. The peaks at 613.7 and 613.3 nm are assigned to A_2 and A_2'; the peak at 609.7 nm is assigned to the unresolved A_1 and A_1' absorptions. Visible photoconversion studies showed that A_1 and A_1' correspond to the red and the blue side of the singlet, respectively.

The two tautomers in the A site in *n*-hexane-d_{14} have the same splitting as for the A site in *n*-hexane; these A sites are probably

---

[9] Butenhoff, T. J.; Moore, C. B. *J. Am. Chem. Soc.* **1988**, *110*, 8336.

[10] Limbach, H. H. Private communication.

[11] Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980.

[12] van Dorp, W. G.; Soma, M.; Kooter, J. A.; van der Waals, J. H. *Mol. Phys.* **1974**, *28*, 1551.

[13] Voelker, S.; Macfarlane, R. M.; Genack, A. Z.; Trommsdorff, H. P.; van der Waals, J. H. *J. Chem. Phys.* **1977**, *67*, 1759.

[14] Conn, G. K. T.; Avery, D. G. *Infrared Methods*; Academic Press: New York, 1960; p 18.

[15] Byer, R. L.; Herbst, R. L. In *Nonlinear Infrared Generation*; Shen, Y. R., Ed.; Springer-Verlag: New York, 1977; p 81.

[16] Völker, S.; van der Waals, J. H. *Mol. Phys.* **1976**, *32*, 1703.

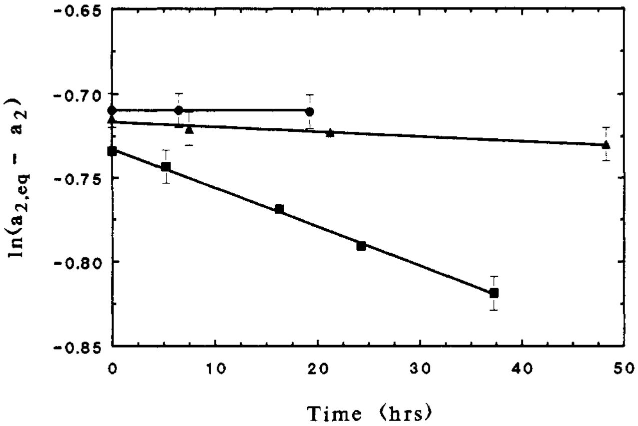

Figure 3. Relative rates of tautomer conversion from Nernst glower irradiation. Circles are $3250 < \nu_{\text{phot}} < 3680$ cm^{-1}, triangles are $4000 < \nu_{\text{phot}} < 5100$ cm^{-1}, and squares are $5630 < \nu_{\text{phot}} < 7700$ cm^{-1}. The slopes of the least-squares-fit lines correspond to $k_1 + k_2$ equal to $(0.5 \pm 8) \times 10^{-4}$, $(3 \pm 4)\ 10^{-4}$, and $(2.3 \pm 0.5) \times 10^{-3}$ h^{-1}, respectively.

the same. It is not known why there is a second site in the deuterated hexane. Simple thermal experiments were performed to elucidate the nature of the second site. A single tautomer (either A_2 or A_2') was burned away with the visible laser, and the refrigerator was turned off. The sample was allowed to warm up to a given temperature, and the refrigerator was restarted, cooling the sample back to 12 K. It was found that the two sites interconvert on a minute time scale at temperatures above 30 K. Fluorescence excitation spectra show that the sites coalesce to one site at temperatures above 40 K. The tautomers thermally interconvert on a minute time scale only when the temperature exceeds 100 K, which implies that the barrier for tautomer interconversion is much larger than the barrier to site interconversion.

The near-infrared-induced tautomerization of H_2P was first investigated by using a Nernst glower photolysis source and infrared band-pass interference filters. Three spectral regions were investigated, each corresponding to known porphine IR absorptions: (I) N–H stretch fundamental region ($3250 < \nu_{\text{phot}} < 3680$ cm^{-1}), (II) combination band region ($4000 < \nu_{\text{phot}} < 5100$ cm^{-1}), and (III) $2\nu_{\text{NH}}$, a combination band consisting of one quantum of the NH symmetric stretch and one quantum of the NH antisymmetric stretch ($5630 < \nu_{\text{phot}} < 7700$ cm^{-1}). Figure 2b shows the excitation spectrum after the A_1 and A_1' tautomers have been photoconverted to A_2 and A_2' with visible light. Figure 2c shows the same sample after 37-h Nernst glower irradiation with $5630 < \nu_{\text{phot}} < 7700$ cm^{-1}. There is clearly tautomer interconversion from this irradiation.

In the broad-band photolysis, both tautomers are expected to absorb equally and the tautomerization kinetics can be described by

$$A_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2 \tag{1}$$

where A_1 and A_2 are the two tautomers, and k_1 and k_2 are the rates for the forward and reverse reactions in the presence of the IR radiation. The integrated rate equation can be written as

$$\ln\,(a_{2,\text{eq}} - a_2) = \ln\,(a_{2,\text{eq}} - a_{2,0}) - (k_1 + k_2)t \tag{2}$$

where a_1 and a_2 are the mole fractions of tautomers 1 and 2, $a_{2,\text{eq}}$ is the steady-state mole fraction of tautomer 2 in the presence of IR, and $a_{2,0}$ is the initial mole fraction of tautomer 2. The steady-state mole fraction is assumed to be 0.5 for the infrared-induced tautomerization.

Figure 3 shows the plot of the tautomer conversion vs time for the three different photolyses; the slope of the lines is equal to $-(k_1 + k_2)$. No tautomer interconversion is observed from irradiation on the NH stretch fundamental band, and photolysis on the $2\nu_{\text{NH}}$ region causes greater interconversion than photolysis over the stretch plus bend combination bands. The null result coupled with the positive results shows that the tautomer interconversion is clearly a result of the irradiation and not caused by a dark reaction or interconversion while probing with the visible laser. It is possible that heating of the matrix is causing the tautomer interconversion, but it should be noted that the *n*-hexane-d_{14} absorptions are much stronger in the photolysis II region than in the photolysis III region (CD stretch first overtone vs the CD stretch second overtone), which is evidence that the interconversion is a result of H_2P absorption and not hexane absorption.

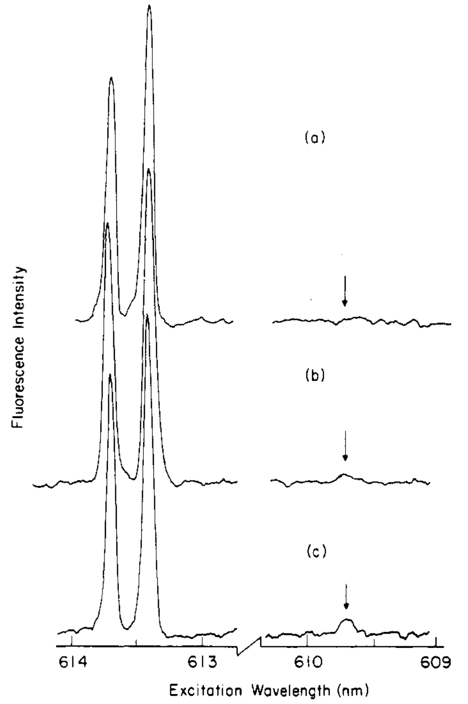

Figure 4. (a) Spectrum taken after burning away most of the A_1 and A_1' tautomers (arrow). (b) The same sample after 30 min of 3.3 mJ/pulse OPO photolysis at 6480 cm^{-1} shows no significant increase in A_1. (c) Irradiation for an additional 30 min with 2.7 mJ/pulse at 6464 cm^{-1} gives a significant amount of A_1 product.

The absorption spectrum of tetraphenylporphyrin dissolved in CCl_4 has absorption bands between 6300 and 6600 cm^{-1} which vanish upon deuteration of the two inner hydrogens.[17] These bands are assigned to excitations of two quanta of NH stretch. The corresponding H_2P absorption is expected to be similar. The $2 \rightarrow 1$ tautomer conversion action spectrum was measured in 8-cm^{-1} steps between 6300 and 6600 cm^{-1}. First the A_1 and A_1' tautomers were depleted by irradiation with the visible laser. The sample was then irradiated for 10–20 min at each wavelength with the signal beam from the OPO, and the sample was probed. Only a few photolysis wavelengths produced tautomer conversion with a signal-to-noise ratio greater than one: near 6360, 6464, and 6530 cm^{-1}. The regions near 6464 and 6530 cm^{-1} were investigated with longer photolysis times. Figure 4 shows the selective nature of the photolysis. Photolysis at 6480 cm^{-1} induces little or no $2 \rightarrow 1$ tautomer interconversion while a similar photolysis at 6464 cm^{-1} clearly induces $2 \rightarrow 1$ interconversion. Figure 5 shows that irradiation at 6530 cm^{-1} causes interconversion of $2 \rightarrow 1$ but does not cause interconversion of $1 \rightarrow 2$. However, $1 \rightarrow 2$ conversion is observed for irradiation at 6522 cm^{-1}. This is good evidence that the interconversion is not caused by bulk hexane heating and that the absorption peaks of the two tautomers are between 4 and 15 cm^{-1} apart. This is reasonable, for it has been observed that tautomers of H_2P in rare gas matrices have infrared absorption shifts of about 5 cm^{-1}.[18] Figure 6 shows the result of another experiment that proves that the infrared-induced tautomerization is due to porphine absorption and not hexane absorption. Only tautomer 2 of the A site was burned away with the visible laser. Irradiation of the sample at 6530 cm^{-1} did not

---

(17) Limbach, H. H.; Rumpel, R.; Zachmann, G. Unpublished results.
(18) Radziszewski, J. G.; Waluk, J.; Michl, J. *Chem. Phys.* **1989**, *136*, 165.

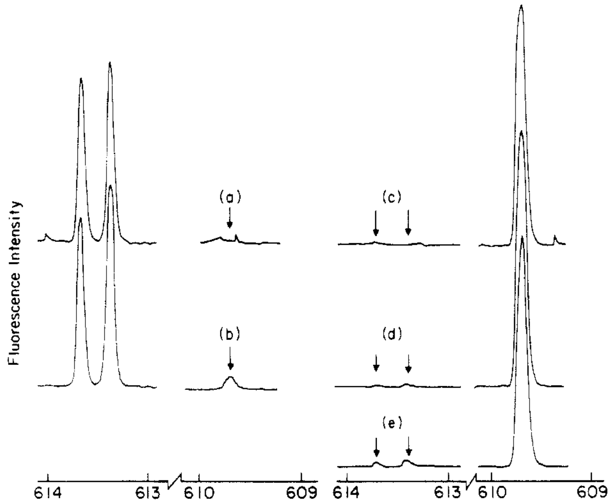

Figure 5. (a) Spectrum taken after burning away most of the A_1 and A_1' tautomers (arrow). (b) The same sample after 200 min of 2.5 mJ/pulse OPO photolysis at 6530 cm^{-1} shows significant A_1 yield. (c) Spectrum after burning away the A_2 and A_2' tautomers (arrows). (d) The same sample after 200 min of 3.5 mJ/pulse OPO photolysis at 6530 cm^{-1} shows no A_2 or A_2' yield. (e) An additional 200 min of 3.0 mJ/pulse OPO photolysis at 6522 cm^{-1} shows clear A_2 and A_2' yield.

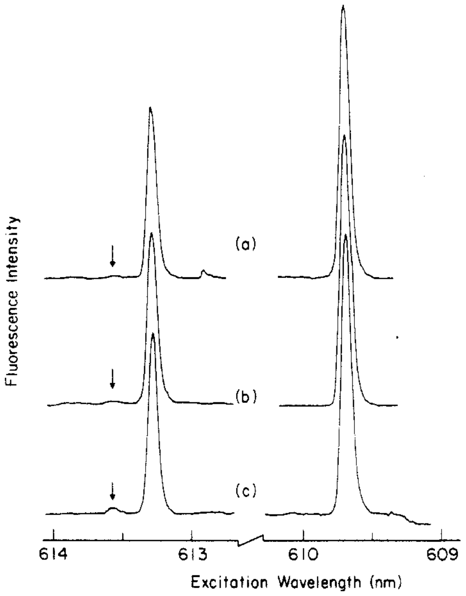

Figure 6. (a) Spectrum after burning away most of the A_2 tautomer (arrow). (b) The same sample after 30 min of 8.6 mJ/pulse OPO photolysis at 6530 cm^{-1} shows no A_2 yield. (c) An additional 30 min of 8.3 mJ/pulse OPO photolysis at 6522 cm^{-1} produces A_2.

interconvert either the tautomers or the sites; irradiation at 6522 cm^{-1} did interconvert the tautomers but *not* the sites. It is known from the thermal studies that the barrier to the site interconversion is less than 1000 cm^{-1}, which is much lower than the barrier to the tautomer interconversion; thus matrix heating, bulk or local, is expected to interconvert the sites much more readily than the tautomers, which is not observed. Clearly, the near-infrared-induced tautomer conversion is due to H_2P absorption and not to bulk or local heating of the sample.

The quantum yield ϕ for the infrared-induced reaction is calculated from the expression

$$\phi = kN_A/(\epsilon N_{ph}\nu_{fwhm} \ln 10) \qquad (3)$$

where weak reactant absorption is assumed; N_A is Avogadro's number. The rate constant k is derived from fitting the growth curve of the tautomer being produced to a first-order rate law. N_{ph} is the photon flux incident on the sample in units of photons cm^{-2} s^{-1} per wavenumber. The quantity ν_{fwhm} is either the photolysis laser bandwidth or the absorption line bandwidth, whichever is smaller. Limbach and co-workers have measured the infrared and near-infrared[8,17] spectra of tetraphenylporphyrin, and the porphine spectrum is expected to be similar. From their results, the extinction coefficient ϵ [$\epsilon = (1/Cl) \log (T_0/T)$] for the N–H stretch fundamental is estimated to be 20–30 L mol^{-1} cm^{-1} with a 23-cm^{-1} (fwhm) bandwidth. The N–H fundamental intensity is 60 ± 20 times more intense than the $2\nu_{NH}$ band.[17] The extinction coefficient ϵ for the $2\nu_{NH}$ absorption is then estimated to be 1.2–3.4 L mol^{-1} cm^{-1} for an assumed fwhm bandwidth of 5 cm^{-1} in the hexane matrix. With this value of ϵ, the quantum yield for the reaction of the A_2 tautomers converting to the A_1 tautomers upon OPO irradiation at 6530 cm^{-1} is 3×10^{-4} to 8×10^{-4}.

Discussion

The primary question is, how does energy flow from the initially excited vibrational state(s) through porphine modes to the bath consisting of the matrix phonons? Is the vibrational energy very quickly distributed among all the porphine vibrational modes, and then transferred to the matrix bath modes, or does the vibrational energy relax along specific pathways? If the vibrational energy relaxes along specific pathways, it could be envisioned that excitation on one particular vibrational coordinate could relax along a path that included modes strongly coupled to the reaction coordinate and a reaction would occur, while excitation on other modes of comparable energy would relax along a path that would bypass the reaction coordinate and no reaction would be observed. This is called mode-specific behavior and in general is not observed. To date, statistical models such as RRKM have been much more successful in describing reaction rates and quantum yields than nonstatistical models.

The RRKM rate of porphine tautomerization is calculated in order to ascertain whether the experimentally estimated quantum yields are consistent with statistical theories or are instead evidence for mode-specific behavior. RRKM theory postulates that the IVR to all of the modes of the system is very fast; i.e., on a time scale short with respect to any observed reaction. If the H_2P and the hexane matrix were considered one very large molecule, the RRKM rate constant for H_2P tautomerization would be zero. It is known that the porphine is weakly coupled to the matrix, so a more realistic application of RRKM theory is to calculate the tautomerization rate for an isolated porphine. The formalism and methods described by Robinson and Holbrook[19] are employed. For a nonrotating isolated molecule with total energy E^*, the RRKM rate of reaction k_a is given by

$$k_a(E^*) = \frac{1}{h\rho^*(E^*)} \sum_{E_v^\dagger=0}^{E^\dagger} P(E_v^\dagger) \qquad (4)$$

where h is Planck's constant, ρ^* is the vibrational density of states of the energized molecule, $E^\dagger$ is the total energy in the active degrees of freedom of the activated complex, $P(E_v^\dagger)$ is the number of vibrational quantum states with a vibrational energy of $E_v^\dagger$, and the sum is the total number of vibrational quantum states of the activated complex with energies up to and including $E^\dagger$.

It is necessary to make simplifying approximations to calculate the sums needed to evaluate eq 4. The first approximation is to treat the vibrations as harmonic oscillators. The second approximation involves calculating the sum of states: summing over the 108 modes of porphine is conceptually easy but in practice too time-consuming. Instead, the method of frequency grouping is applied where the 108 frequencies are gathered into a few groups of degenerate modes; a direct counting of states is performed on the frequency groups with the inclusion of the appropriate degeneracy factors. Normal-coordinate analyses of the 73 in-plane modes have been published, and the frequencies used here are from ref 20. The six frequency groups that are chosen to represent the in-plane vibrations are shown in Table I. The 35 out-of-plane

---

(19) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: London, 1972.

(20) Gladkov, L. L.; Solovyov, K. N. *Spectrochim. Acta* **1985**, *41A*, 1437.

TABLE I: Frequency Groupings and RRKM Calculated Rates[a]

ν, cm^{-1}	ip[b]	c	d
125	2	2	5
343	7	7	7
450	0	21	18
769	8	10	10
1084	21	33	33
1454	21	21	21
3116	14	14	14
ρ^*, states/cm^{-1}		6.8×10^{10}	8.4×10^{11}
$\sum P(E_v^\dagger)$		4.4×10^5	3.1×10^6
k_a, s^{-1}		1.9×10^5	1.1×10^5

[a] $E^* = 6500$ cm^{-1}; $E^\dagger = 2000$ cm^{-1}. [b] The 73 in-plane normal modes only. [c] Out-of-plane modes included; see text. [d] Out-of-plane modes included with three additional 125-cm^{-1} modes.

vibrational modes consist of 12 C–H bending modes, 2 N–H bending modes, and 21 heavy-atom bending modes (C–C–C, C–C–N, etc.). The 12 C–H out-of-plane bending modes are assigned to the 1084-cm^{-1} group, and the N–H bending frequencies are put into the 769-cm^{-1} group. The 21 skeletal out-of-plane modes are assigned a frequency of 450 cm^{-1}, which is consistent with both benzene out-of-plane skeletal vibrational frequencies[21] and H_2P in-plane skeleton deformation frequencies.[20] To check the sensitivity of the calculations on the number of very low frequency modes, an additional frequency grouping is made by arbitrarily changing three of the 450-cm^{-1} modes to 125-cm^{-1} modes. Table I shows both sets of frequency groupings.

The activated complex is assumed to have the same vibrational frequencies as the energized molecule except one mode is lost to the reaction coordinate. The reaction coordinate is presumably some combination of the N–H stretch and bend, and one mode is removed from the 1454-cm^{-1} group to represent the activated complex frequencies. Table I shows the calculated density of states for the energized molecule at a typical OPO photolysis energy of 6500 cm^{-1}. It also lists the activated complex sum of states and the RRKM rates for both sets of frequency groupings, where a reaction barrier of 4500 cm^{-1} is used.[9,10] The calculated values of k_a are very sensitive to the barrier height; increasing the barrier height to 5000 cm^{-1} decreases the calculated value of k_a by an order of magnitude.

The RRKM quantum yield ϕ^{RRKM} for the tautomerization reaction in the matrix is defined as the ratio of the RRKM rate of reaction k_a to the relaxation rate of H_2P vibrational energy to the matrix, k_{nr}. The lifetimes of vibrational levels with $155 < E_{vib} < 1590$ cm^{-1} of S_1 H_2P in an *n*-octane matrix at 4 K have been measured by hole-burning techniques.[22] Values ranging from 0.9 to 44 ps were obtained, with no correlation between vibrational energy and relaxation times. The relaxation time for $E_{vib} = 154$ cm^{-1} is 3.3 ps and is most likely a measure of the porphine vibrational energy transfer rate to the matrix phonons. The density of states at this low vibrational energy is low, and the IVR time to these low frequency modes is expected to be greater than picoseconds. Reasonable values for k_{nr} for S_0 H_2P in a hexane matrix are $\approx 2 \times 10^{10}$ to 1×10^{12} s ($\tau = 1$–50 ps). The corresponding range in ϕ^{RRKM} is 9×10^{-6} to 1×10^{-7}. The smallest value of the quantum yield estimated from the OPO photolysis experiments, 3×10^{-4}, is a factor of 30 times larger than the largest estimate for ϕ^{RRKM}.

It is not prudent to claim that the porphine tautomerization is mode specific or non-RRKM from the comparison of the experimentally estimated quantum yields to the RRKM quantum yields; there are too many uncertainties in the analysis to make such a strong statement. However, porphine tautomerization does appear to be a good candidate to exhibit non-RRKM behavior. The best test would be to compare the relative quantum yields for excitation of C–H overtones and combination bands to excitation of N–H overtones and combination bands of comparable energy. It is expected that N–H stretching and bending motions are coupled more strongly to the reaction coordinate than the C–H motions which are initially confined to the outskirts of the skeleton, far away from the inner hydrogens. It may be better to perform this experiment in a rare gas matrix than in a Shpol'skii matrix. It has been shown that the infrared and visible absorption lines of H_2P in rare gas matrices are very narrow and that there is a frequency shift for the different tautomers of a given site.[18] The big advantage of the rare gas matrices is the optical transparency of the matrix, which would allow the measurement of the infrared absorption spectrum of the porphine in the matrix. The present experiments were terminated when the Nd:YAG laser pumping the OPO failed to function on a regular basis.

Conclusion

Nernst glower irradiation in the regions of $4000 < \nu < 5100$ cm^{-1} and $5630 < \nu < 7700$ cm^{-1} induces the tautomerization of free-base porphine imbedded in a *n*-hexane-d_{14} matrix. Narrow-band laser irradiation studies in the NH symmetric and antisymmetric stretch combination band region ($6300 < \nu < 6600$ cm^{-1}) show that the near-infrared-induced tautomerization occurs at select wavelengths. Tautomer conversion in the absence of site conversion is strong evidence that the observed photochemistry is due to porphine absorption and not hexane absorption. The estimated quantum yield for the tautomerization is 1–3 orders of magnitude larger than the quantum yield calculated with RRKM theory. Further experiments, such as CH overtone excitation, are needed to determine whether there is mode-specific behavior in this reaction.

Acknowledgment. We thank Prof. Herbert L. Strauss for helpful discussions on the fundamental frequencies of porphine and Dr. J. G. Radziszewski and Prof. J. Michl for a preprint of ref 18. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. T.J.B. acknowledges support from the National Science Foundation in the form of a predoctoral fellowship.

Registry No. H_2P, 101-60-0; *n*-hexane-d_{14}, 21666-38-6.

---

(21) Herzberg, G. *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945; pp 363-367.

(22) Voelker, S.; Macfarlane, R. M. *Chem. Phys. Lett.* **1979**, *61*, 421.