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THE NEAR-INFRARED PHOTOCHEMISTRY OF PORPHINE IMBEDDED IN AN N-HEXANE MATRIX

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

Department of Chemistry, University of California, Berkeley, California 94720,
and Materials and Chemical Sciences Division of the Lawrence Berkeley Laboratory,
Berkeley, California 94720 USA.

[a]Institut für Physikalische Chemie, Universität Freiburg,
Albertstr. 21, D-7800 Freiburg i. Br., West Germany

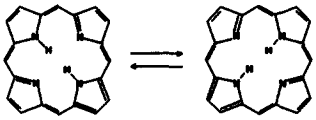
Abstract: The near-infrared induced tautomerization of free-base porphine incorporated in a *n*-hexane-d_{14} matrix is reported. Nernst glower irradiation on the NH stretch fundamental does not induce tautomerization, but irradiation in the regions $4000 < \nu < 5100$ cm^{-1} and $5630 < \nu < 7700$ cm^{-1} does induce tautomerization. Narrowband (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 porphine absorption and not hexane absorption. The estimated quantum yield of 3×10^{-5} for 6530 cm^{-1} irradiation is at least one order 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, but to date only a small number of infrared single photon reactions have been observed [1-3]. These include interconversion of rotamers such as HONO and CH_2FCH_2OH, reactions and isomerization of $FeCO_4$, and bimolecular reactions of small organic molecules with F_2. The weak coupling between the guest molecule and the matrix allows intramolecular vibrational relaxation (IVR) in the guest to compete with vibrational energy transfer from the guest to the matrix. There is hope that selective excitation of fundamental or low overtone vibrations that are strongly coupled to the reaction coordinate will lead to mode-selective chemical reactions [2,3].

Here, the initial results of the near-infrared induced tautomerization of free-base porphine (H_2P) imbedded in a *n*-hexane-d_{14} matrix are reported. This experiment was inspired by Hennig and Limbach's NMR studies on tetraphenylporphyrin which show that the barrier to tautomerization is low enough to be accessible by excitation of one or two quanta of the N-H stretch [4]. It is tantalizing to speculate that the N-H stretch is strongly coupled to the reaction coordinate which would make porphyrins ideal candidates to exhibit mode-specific behavior.

At 12 K, porphine occupies two sites in the *n*-hexane-d_{14} matrix. For each site, the porphine has two orientations, or tautomers, that differ by an exchange of the two inner hydrogens from one pair of nitrogens to the other [5]. The barrier to tautomerization is 4500-5500 cm^{-1} [6], 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.



(1)

The two tautomers have different crystal field effects in the matrix, which cause their $S_1 \leftarrow S_0$ absorptions to differ by 100 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 photochemically converted to the other tautomer of that site by irradiation on its 0-0 band, and vice versa [7] (Fig. 1).

EXPERIMENTAL

The photolysis experiments were carried out with the sample at 12 K. The H_2P concentration in the samples is estimated to be $\approx 10^{-6}$ M. The probe excitation light was provided by an argon ion pumped continuous wave dye laser (1 cm^{-1} fwhm bandwidth, 30-60 mW) and fluorescence with $\lambda > 645$ nm was detected and recorded as a function of excitation wavelength. When probing the sample, the dye laser was attenuated with a 10^{-4} neutral density filter to avoid the photocon-

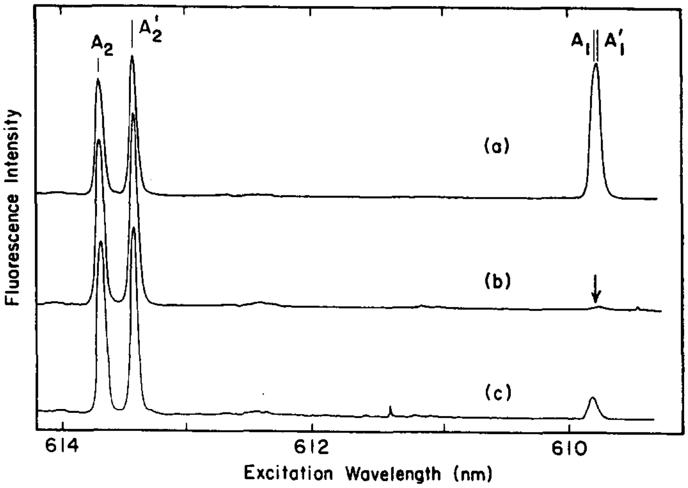


Fig. 1. (a) Fluorescence excitation spectrum of H_2P in n-hexane-d_{14}. (b) Spectrum taken after burning away most of the A_1 and A'_1 tautomers. (c) Spectrum after 37.2 hrs Nernst glower irradiation with $5630 < \nu_{phot} < 7700$ cm^{-1}. All spectra are recorded with the sample at 12 K and are not normalized for incident laser power.

version of the tautomers.

Broadband infrared radiation was provided by a Nernst glower with suitable infrared bandpass filters. A Nd:YAG pumped optical parametric oscillator (OPO) was used for narrowband infrared photolysis from 6300 to 6550 cm^{-1}. The OPO was operated at 10 Hz and had a typical signal output power of 3-9 mJ per 10 ns (fwhm) pulse and an 8 cm^{-1} fwhm bandwidth. The average flux on the sample per unit cm^{-1} bandwidth was 3 to 9×10^{17} photons cm^{-2} s^{-1}.

RESULTS

Figure 1a 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. 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 labelled A and A′ and a subscript 1 or 2 denotes the two tautomers [7]. It is not known why there is a second site in the deuterated hexane. It was found that the two sites interconvert to each other on a minute timescale at matrix temperatures above 30 K, and coalesce to one site at temperatures above 40 K. The tautomers thermally interconvert on a minute timescale only when the temperature exceeds 100 K [6], 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 using a Nernst glower photolysis source and infrared bandpass filters. Three spectral regions were investigated, each corresponding to known porphine IR absorptions: (I) N-H stretch fundamental region ($3250 < \nu_{phot} < 3680$ cm^{-1}), (II) combination band region ($4000 < \nu_{phot} < 5100$ cm^{-1}), and (III) $2\nu_{NH}$, a combination band consisting of 1 quantum of the NH symmetric stretch plus 1 quantum of the NH antisymmetric stretch ($5630 < \nu_{phot} < 7700$ cm^{-1}). Figure 1b 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 1c shows the same sample after 37 hrs Nernst glower irradiation with $5630 < \nu_{phot} < 7700$ cm^{-1}. There is clearly tautomer interconversion from this irradiation.

In the broadband photolysis, both tautomers are expected to absorb equally and the integrated rate equation can be written as

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

where a_1 and a_2 are the mole fractions of tautomers 1 and 2, $a_{2,eq}$ is the steady state mole fraction of tautomer 2, $a_{2,o}$ is the initial mole fraction of tautomer 2, and k_1 and k_2 are the rate constants for the forward and reverse reactions. The tautomer mole fractions are determined from the integrated fluorescence peaks.

Figure 2 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 $2\nu_{NH}$ region causes greater interconversion than photolysis over the 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.

The absorption spectrum of tetraphenylporphyrin dissolved in CCl_4 has strong absorption bands between 6300 and 6600 cm^{-1} which are assigned to excitations of two quanta of the NH

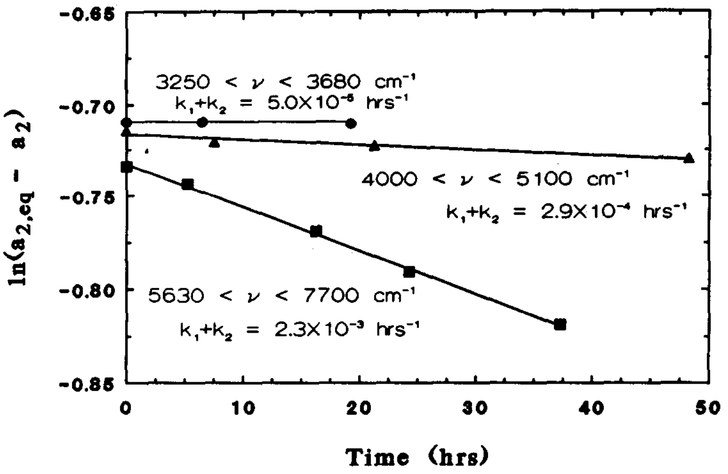


Fig. 2. Relative rates of tautomer conversion from Nernst glower irradiation.

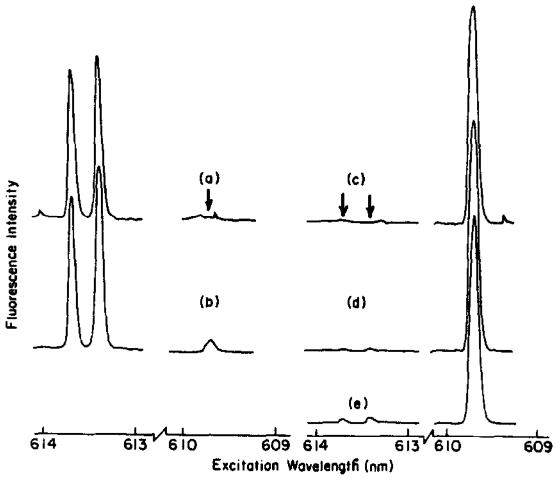


Fig. 3. (a) Spectrum taken after burning away most of the A_1 and A_1' tautomers. (b) The same sample after 200 min of 2.5 mJ/pulse OPO photolysis at 6530 cm^{-1} shows significant A_1 and A_1' yield. (c) Spectrum after burning away the A_2 and A_2' tautomers. (d) The same sample after 200 min of 3.5 mJ/pulse OPO photolysis at 6530 cm^{-1} shows no 2←1 yield. (e) The same sample after an additional 200 min of 3.0 mJ/pulse OPO photolysis at 6522 cm^{-1} clearly shows A_2 and A_2' yield.

stretch [8]. The corresponding H_2P absorption is expected to be similar. OPO photolysis was used to measure the 2→1 tautomer conversion action spectrum in 8 cm^{-1} steps between 6300 and 6600 cm^{-1}. Tautomer conversion occurred with photolysis at only a few wavelengths: near 6360, 6464, and 6530 cm^{-1}. The regions near 6464 cm^{-1} and 6530 cm^{-1} were investigated with longer photolysis times. Figure 3 shows that irradiation at 6530 cm^{-1} causes interconversion of 2→1, but does not cause interconversion of 1→2. However, 1→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 two tautomers have slightly different absorption peaks. 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} [9].

Another experiment was performed that strongly suggests 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 interconvert either the tautomers or the sites, while 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 much lower than the barrier to the tautomer interconversion, and matrix heating is expected to interconvert the sites much more readily than the tautomers. The selective tautomer interconversion in the absence of site interconversion implies that the near-infrared induced tautomer conversion is due to H_2P absorption and not to bulk heating of the sample. 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 estimated to be 3×10^{-5}.

DISCUSSION

The primary question is how does energy flow from the initially excited vibrational state(s) to the reaction coordinate, to the other vibrations, and 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 relaxed 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 non-statistical models.

The RRKM rate of porphine tautomerization is calculated in order to ascertain if the experimentally estimated quantum yields are consistent with statistical theories or, are instead, evidence for mode specific behavior. RRKM theory states that the intramolecular energy transfer (IVR) among all of the modes of the system is very fast; i.e. on a time scale short with respect to any observed reaction [10]. If the H_2P and the hexane matrix were considered one very big 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 molecule. The RRKM quantum yield ϕ^{RRKM} for the tautomerization reaction in the matrix is defined as the ratio of the RRKM rate of reaction to the relaxation rate of H_2P vibrational energy to the matrix. The value of the relaxation rate has not been measured, but the relaxation time of the H_2P low frequency modes (≈ 100 cm^{-1}) to the matrix is expected to be on the order of picoseconds (1-100 ps). When a barrier of 5000 cm^{-1} is assumed, reasonable values for ϕ^{RRKM} range from 10^{-6} to 10^{-9}, with a best estimate of 1×10^{-7}. The calculated values of ϕ^{RRKM} are very sensitive to the barrier height; a barrier height change of 500 cm^{-1} changes the calculated value of ϕ^{RRKM} by an order of magnitude.

The quantum yield estimated from the OPO photolysis experiments, 3×10^{-5}, is about 300 times larger than the best estimate for ϕ^{RRKM}, and is a factor of 30 times larger than the largest reasonable estimate for ϕ^{RRKM}. We do not 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. These 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 H_2P imbedded in a *n*-hexane-d_{14} matrix. Narrowband 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 porphine absorption and not hexane absorption. The estimated quantum yield for the tautomerization is 30 to 3×10^{4} times larger than the quantum yield calculated with RRKM theory. Further experiments, such as CH overtone excitation, are needed to determine if there is mode-specific behavior in this reaction.

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