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Light-induced intermolecular proton transfer from gas-phase ions to neutral molecules

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Abstract

It is shown by use of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry that photoexcitation of protonated naphthalene by visible laser light of 488 nm can effect a proton transfer from this ion to acetonitrile. The reaction of the ground state reaction partners is endoergic by 31 kJ/mol. (Int J Mass Spectrom 182/183 (1999) 7–12) © 1999 Elsevier Science B.V.

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1. Introduction

Reactions between ions and molecules in the gas phase, in which the ions and molecules are in their ground state, have been studied extensively by use of various experimental methods, in particular flowing afterglow (FA) [1–3] and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry [4,5]. These studies have provided a wealth of information on reaction mechanisms and kinetics [6–13], ion structures [14,15], and quantitative thermodynamic data including proton and electron affinities of neutral species and heats of formation of both ions and neutral molecules in the gas phase [16,17].

Very limited research, however, has been devoted to reactions between electronically and/or vibrationally excited ions and neutral molecules in the gas phase. In this area of research a number of elegant studies have been published in which the electronically and/or vibrationally excited state population of small ions, such as NO^+, $O_2^{\cdot+}$, $HCl^{\cdot+}$, and HCO^+, has been probed via an ion/molecule reaction [18–20]. The ion/molecule reaction is chosen such that it is thermodynamically allowed only for excited ions. This serves to chemically monitor the internal energy of the ions and has been termed the ion monitoring technique [18]. Using this technique in a triple FTICR spectrometer, the vibrationally excited state population and associated radiative lifetimes of CF^+ [21] and NO^+ [19] have been determined by charge transfer with suitable monitor molecules, while those of HCO^+ [19] have been obtained by monitoring proton transfer to suitable molecules.

In the present study protonated naphthalene has

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Dedicated to the late Professor Ben Freiser for his friendship and his exciting contributions to gas phase ion chemistry.

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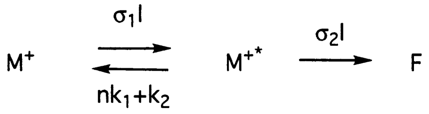
been excited in the gas phase with use of light from an Argon ion laser with the aim to observe a proton transfer reaction that in the absence of excitation would be endothermic. The motivation for such research derives from the present widely applied method of matrix assisted laser desorption ionization (MALDI) in the analysis of large molecules [22,23]. It has been suggested that excited neutral matrix molecules or ions produced by photon absorption in the gas phase following the initial desorption process may play a role in the MALDI ionization process [24]. Such excited species have an increased acidity and could therefore in part account for the formation of protonated analyte molecules in MALDI through proton transfer in a gas phase ion/molecule reaction.

Following a description of the conditions for photochemical experiments on gas phase ions in an FTICR mass spectrometer, experimental details will be given. Subsequently the results obtained will be presented and discussed.

2. Conditions for photochemical experiments on gas phase ions in an FTICR mass spectrometer

When studying photochemical reactions of ions in an FTICR cell, the experimental conditions must be chosen rather carefully. First of all, the ions must absorb light in the wavelength region used and the resulting excited state should be below the dissociation threshold of the ions. It is well known [25–27] that, in these cases, the photoexcited ions often have a lifetime sufficiently long to absorb a second photon and to dissociate by a two- (or multi-) photon process. This long lifetime, of course, is also required to make bimolecular reactions of the photoexcited ions possible. In general, photochemical reactions of gas-phase ions therefore will be in competition with two- (or multi-) photon dissociation processes.



Scheme 1

The reaction scheme for a pure two-photon dissociation process is shown in Scheme 1. In this scheme F represents the fragment ions plus neutral species. I is the light intensity, σ_1 and σ_2 are the cross sections for absorption of the first and the second photon, n is the density of neutral molecules, and k_1 and k_2 are the rate constants for collision-induced and collisionless (IR emission) relaxation of the photoexcited ions [25,26]. According to previous work [25,26] the decay of the ion abundance is singly exponential (Eq. 1).

$$M(t,I)/M(t,0) = \exp[-I^2\sigma_1\sigma_2/\{nk_1 + k_2 + I(\sigma_1 + \sigma_2)\} \quad (1)$$

Here $M(t,I)$ and $M(t,0)$ are the ion abundances after t seconds with and without irradiation. It follows from Eq. 1 that $-I/1\mathrm{n}\{M(t,I)/M(t,0)\}$should be linear with 1/I (Eq. 2).

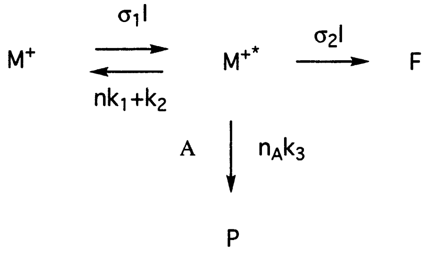
$$-I/1\mathrm{n}\{M(t,I)/M(t,0)\} = (nk_1 + k_2)/I\sigma_1\sigma_2 + (\sigma_1 + \sigma_2)/\sigma_1\sigma_2 \quad (2)$$

Extension of Scheme 1 to include photochemical reactions with a substrate molecule A leads to Scheme 2 where P are the bimolecular reactions products, n_A is the density of molecules A, and k_3 is the bimolecular rate constant for reaction of ions M^{+*} with molecules A.

It is obvious from Scheme 2 that the ratio of product and fragment ion abundances is given by Eq. 3.

$$F/P = \sigma_2 I/n_A k_3 \quad (3)$$

In order to observe photochemical reactions, it is therefore essential that the relative pressure of mole-



Scheme 2

cules *A* is as high as possible in the FTICR experiments. In contrast, competing reactions of ions $M^{\cdot +}$ with its neutral precursor should be suppressed as much as possible. Since the FTICR spectrometer used in the present experiments does not have an external ion source, the pressure of the precursor molecules therefore has been kept close to 10^{-9} Torr. In addition, to make a clear distinction between reactions of ground and excited state ions, it appeared to be important to thermalize ions *M* as much as possible before irradiation was started.

3. Experimental

The experiments were performed with a laboratory-built Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The major components of this instrument are a 2.5 cm cubic cell in a 1.4 Tesla 12-inch magnet, a Motorola MVME133 computer, a home-built microcomputer that produces all the necessary pulses and controls, a Wavetak/Rockland model 5110 frequency synthesizer and laboratory-built stored waveform inverse Fourier transform (SWIFT [4]) unit. The protonated naphthalene species were isolated in the FTICR cell by use of the SWIFT method. For excitation of the ions with visible light a 4 W Spectra-Physics Stabilite 2017 argon ion laser was used. The light beam (488 nm) from the laser was expanded to a diameter close to 2.5 cm to ensure irradiation of all ions present in the ICR cell and was controlled by a shutter opened and closed by a pulse from the microcomputer.

In the photodissociation measurements protonated naphthalene species were prepared from naphthalene by proton transfer from CH_5^+ generated from methane which reaction is exothermic by 264 kJ/mol. In the photochemical experiments these ions were obtained as fragment ions from 1-methyl-3,4-dihydronaphthalene at electron ionizing energies of 20–25 eV. The latter compound was prepared according to the literature [27].

Collision-induced dissociation spectra of protonated naphthalene, prepared in a chemical ionization source by protonation of naphthalene with methane as reactant gas and by electron ionization induced fragmentation of 1-methyl-3,4-dihydronaphthalene, were obtained with use of a four sector Jeol SX/SX 102A tandem instrument (Jeol Ltd. Akishima, Tokyo, Japan). Following selection of the main ion beam by the first *B* and *E* sectors, collision-induced dissociation experiments were performed in the third field-free region using argon as a target gas at such a pressure that the signal of the mass selected ion beam was reduced to 50% of its original intensity. The obtained collision-induced dissociation spectra appeared to be practically identical.

4. Results and discussion

The lifetimes of excited aromatic hydrocarbon (radical) cations are known to be in the order of a few hundred ms [25,26], which matches nicely the time scale of the FTICR method used in the present study.

Initially attempts were made to perform experiments with photoexcited protonated benzene, but no reaction could be observed, probably because the ions do not absorb 488 nm light, considering the reported calculated absorption spectra [28,29].

A more satisfactory result has been the generation of sufficiently abundant protonated naphthalene, which was obtained in the FTICR cell from either protonation of naphthalene by CH_5^+ formed from methane or electron ionization induced fragmentation of 1-methyl-3,4-dihydronaphthalene. The ions prepared by either method have the same structure, as indicated by their corresponding collision-induced dissociation spectra (see Experimental).

Most of the experiments have been performed with 1-methyl-3,4-dihydronaphthalene as precursor of protonated naphthalene for practical reasons (no mixing of two gases required as in the case of protonation of naphthalene by CH_5^+ formed from methane). It should be emphasized, however, that similar results from the experiments using FTICR have been obtained with either method. Prior to excitation of the protonated naphthalene species by laser light, their behavior in the absence of light and in the presence of both its precursor molecule 1-methyl-3,4-dihydronaphthalene

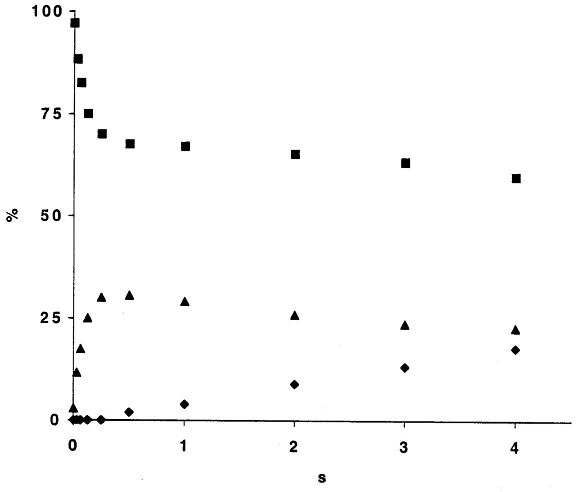


Fig. 1. Thermalization of protonated naphthalene (■), generated from 1-methyl-3,4-dihydronaphthalene upon 20 eV electron ionization, by collisions with its precursor and acetonitrile as a function of time. Partial pressures were 1 × 10^{-9} Torr for 1-methyl-3,4-dihydronaphthalene and 1.5 × 10^{-7} Torr for acetonitrile. ▲ = protonated acetonitrile; ◆ = protonated 1-methyl-3,4-dihydronaphthalene.

and acetonitrile was monitored as a function of time. The observations made are presented in Fig.1.

As can be seen from Fig.1, after about 500 ms under the applied experimental conditions (see Secs. 2 and 3) the original protonated naphthalene species have been thermalized by nonreactive collisions and no longer transfer a proton to acetonitrile. This time has been used as “waiting period” to achieve removal of electron ionization excited protonated naphthalene species prior to illumination of the remaining and thermalized protonated naphthalene molecules by laser light in the experiments described below. To reduce proton transfer from protonated naphthalene in both its ground and excited state to its neutral precursor 1-methyl-3,4-dihydronaphthalene, the pressure of the latter was held at a 100-fold lower pressure than that of acetonitrile.

Subsequently, it was first shown that protonated naphthalene photodissociates via a pure two-photon dissociation process. In this photodissociation process protonated naphthalene loses a hydrogen atom. The amount of this hydrogen atom loss has been measured at different intensities of the laser by measuring the corresponding peak height with the laser on and off.

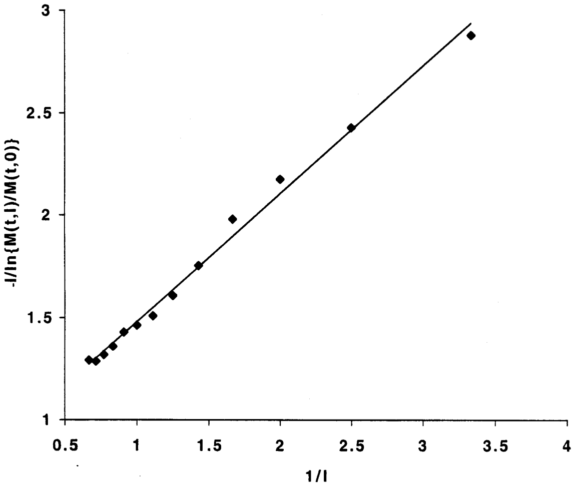


Fig. 2. Fraction of two-photon dissociating protonated naphthalene ions as a function of light intensity at 488 nm plotted according to Eq. 2 (see text). Partial pressures were 2 × 10^{-8} Torr for naphthalene and 6 × 10^{-8} Torr for the protonated reagent gas methane.

As expected for a pure two-photon dissociation process, a plot of $-I/\ln\{M(t,I)/M(t,0)\}$versus $1/I$ should give a straight line [see Eq. (2) in Sec. 2] as is observed indeed (see Fig 2).

This means that absorption of one photon leads to photoexcited protonated naphthalene with a sufficiently long lifetime for a second photon to be absorbed. The question is whether this photoexcited protonated naphthalene is in a singlet or triplet excited state. A few studies have been published in which the $\lambda_{\max}$ of singlet and triplet excited states of protonated naphthalene have been calculated and measured [28–31]. The $\lambda_{\max}$ of the first excited singlet state of protonated naphthalene is at 410 nm and has a shoulder extending up to 500 nm which covers the 488 nm wavelength of the Argon ion laser used. It has also been shown that protonated naphthalene in glasses exhibits a phosphorence spectrum [31], indicating an intersystem crossing from the singlet excited state to the triplet state. It is therefore very plausible that in the present study the second photon is absorbed from the triplet, and consequently from a relatively long-lived, excited state of protonated naphthalene.

In an experiment done in the presence of acetonitrile, photo-excited protonated naphthalene has been found to be capable to transfer a proton to this

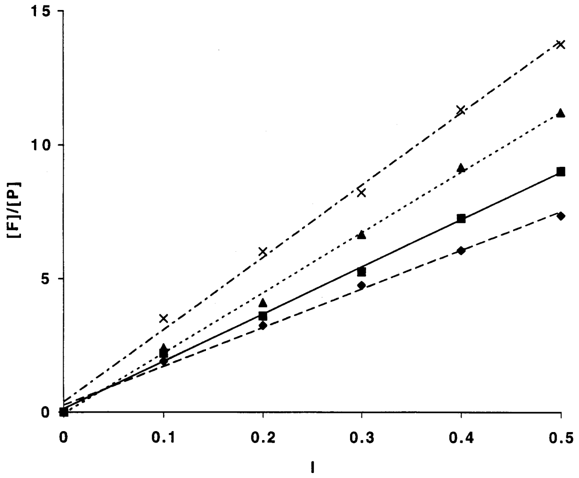


Fig. 3. Ratio of abundances of photofragment ions of protonated naphthalene and its bimolecular product ions ([F]/[P]) as a function of light intensity at 488 nm measured at different pressures and plotted according to Eq. 3 (see text). The partial pressure of 1-methyl-3,4-dihydronaphthalene is 1×10^{-9} Torr and that of acetonitrile 3.8×10^{-7} Torr (◆), 2.8×10^{-7} Torr (■), 2.3×10^{-7} Torr (▲), and 1.9×10^{-7} Torr (x).

molecule. This process does not occur from protonated naphthalene in its ground state.

According to Eq. (3) in Sec. 2, the ratio of abundances of photofragment ions of protonated naphthalene (because of the two-photon dissociation process) and product ions (because of proton transfer to acetonitrile) should depend linearly on the laser light intensity. Fig. 3 shows that this is observed indeed, where the various straight lines have been obtained at different acetonitrile pressures.

A plot of the reciprocal slopes of the straight lines in Fig. 3 versus pressure yields the linear relationship between the ratio of abundances of product and photofragment ions and pressure as shown in Fig. 4.

This is in agreement with Eq. (3) in Sec. 2, which is expressed in terms of number density. Experiments to determine the threshold of proton transfer from photoexcited protonated naphthalene to suitable bases by the bracketing method as well as the effect of aromatic ring substitution are in progress. The results will be reported in future publications.

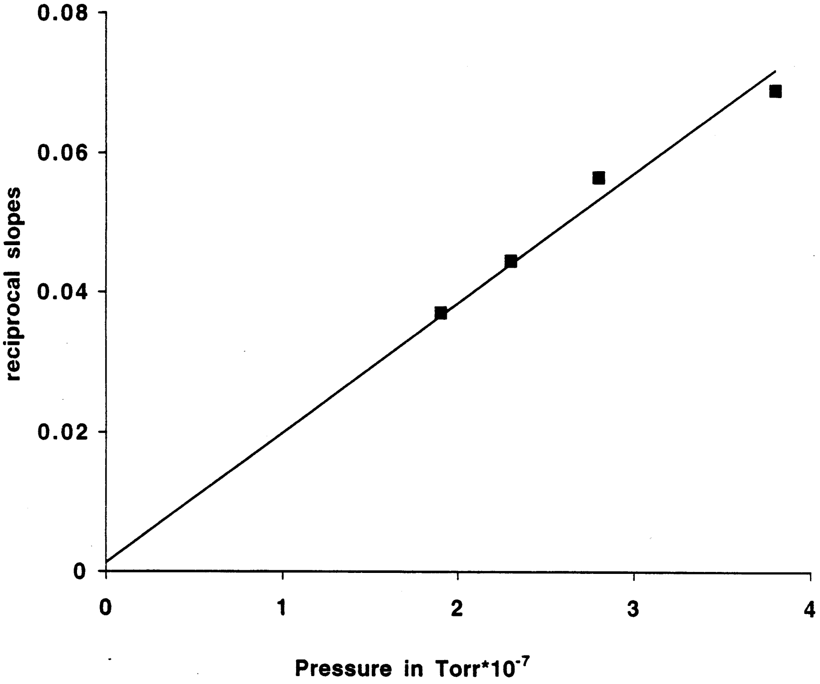


Fig. 4. Reciprocal slopes of the lines in Fig. 3 as a function of pressure (see further text).

5. Conclusion

The present study has shown that visible light can effect proton transfer from ions to neutral molecules in the gas phase. The gas-phase basicity of naphthalene is 31 kJ/mol larger than that of acetonitrile so that photoexcitation by visible light in this particular case studied has enabled to overcome a reaction endoergicity of at least 31 kJ/mol.

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This article is dedicated to the late Professor Ben Freiser for his friendship and his exciting contributions to gas phase ion chemistry.

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