Light-induced proton transfer from gas phase protonated naphthalene and the indene radical cation to reference bases and their associated kinetics

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Publication date
2001

Citation for published version (APA):
A study of light-induced proton transfer from gas phase indene radical cations to reference bases and associated reaction kinetics.

Abstract

By use of Fourier transform ion cyclotron resonance, it is shown that for indene radical cations excited at 514.5 nm, the rate constant for intermolecular proton transfer to 3-pentanone is either about 10 or about 100 times lower than the rate constant for relaxation by collisions with 3-pentanone. From the energy deposited in the indene ions, 0.5 eV is available for proton transfer to a base which seems reasonable when taking into account a complete randomization of the initially deposited energy.

5.1 Introduction

Ground state reactions between ions and molecules in the gas phase have been studied extensively by use of various experimental methods, in particular Flowing Afterglow (FA) [1-3] and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry [4,5]. These studies have provided a wealth of information and a detailed knowledge on ion/molecule reaction mechanisms and kinetics [6-13], ion structures [14,15] and thermodynamic properties [16]. Much less is known, however, about the change of such properties when the ions are excited. For example, the gas-phase reactivity of a number of small excited ions, such as NO⁺, O₂⁺, HCl⁺ and HCO⁺ has been investigated using
the ion monitoring technique [17-19]. The monitoring of such difference in reactivity may shed some further light on at present not fully understood mechanisms of matrix assisted laser desorption ionization (MALDI) [20-27] where pulsed laser light and a chromophore as matrix are used to evaporate and protonate analyte molecules. This protonation of the analyte molecules has been proposed to occur in the gas phase by reaction of the electronically excited matrix molecules with ground state analyte molecules [23]. The ejection of species into the gas phase and possible ionization processes in MALDI mass spectrometry have been described [24]. Recent studies propose multicenter excitation of matrix molecules and charge transfer from neutral excited matrix molecules to other neutral molecules, whereby the generated charged matrix species subsequently protonate the analyte [26-28].

In chapters 3 and 4 and previous articles from this laboratory, the reactions of laser-light excited gas-phase ions were investigated where a proton is transferred from excited indene radical cations or excited protonated naphthalene to reference bases [29,30]. In the study on the indene radical cations [30] it was observed, that the laser-light excited gas-phase ions transfer a proton to reference bases with much lower proton affinities than the ground state proton affinity of the donor, which in the ground state is an endoergic reaction. It appeared that this endoergicity should not be larger than about 50 kJ/mol (=0.5 eV) notwithstanding the 2.41 eV (=514.5 nm) energy deposition into the indene radical cations. In ref. [30] it was suggested that relaxation of the excited (radical) cations after internal conversion to a highly vibrationally excited ground state is much faster than the intermolecular proton transfer and that this could explain the relatively small amount of the total energy deposition available for proton transfer.

In this chapter a model is proposed which has been used to determine experimentally the ratio of the photon absorption cross sections, $\sigma_1/\sigma_2$ of
scheme 5-3 and 5-5 and the ratio of the rate constants of relaxation of and proton transfer from excited indene radical cations.

5.2 Experimental

The experiments were performed with a laboratory-built Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with three inlet systems, a 1.4 T 12-inch Varian magnet used at 1.25 T, and a SWIFT (Stored Waveform Inverse Fourier Transform [31]) unit. The SWIFT unit allows the ejection of unwanted ions at specifically chosen mass ranges during the experiments. The laser light from the argon ion laser (Spectra-Physics Stabilite 2017) enters the FT-ICR cell perpendicular to the magnetic field direction via a shutter, a lens system to broaden the beam so as to cover most of the space of the cubic cell (2.5 cm) through a sapphire window and is reflected by a slightly concave mirror positioned behind the cell. The laser power was adjusted by a calibrated laser power controller at 514.5 nm in the experiments with the indene radical cation. Except for indene-d$_3$, synthesized according to ref [32], all other compounds were commercially available and used without further purification.

Various experiments were performed to determine the rate constants $k_1$, $k_2$ and ratio’s $\sigma_1/\sigma_2$ and $k_4/k_3$ in schemes 5-3 and 5-5 for the indene radical cation which will be discussed in the following section. For a reasonable approximation of $k_1$, indene and indene-d$_3$ were introduced into the cell both at a partial pressure of $2.5\times10^{-8}$ Torr to measure the rate constant for charge transfer between the molecular ion of indene-d$_3$ and its unlabeled neutral. After isolating the indene-d$_3$ radical cation by application of several SWIFT pulses, the abundances of the formed indene radical cation and reacted indene-d$_3$ were measured at several reaction times.
For determining the ratio of $\sigma_1$ and $\sigma_2$ in the pure two-photon dissociation experiments, the typical pulse sequence of the ion formation, ejection and detection was applied as shown in scheme 5-1. Following electron ionization of indene at pressures from $3 \cdot 10^{-8}$ Torr up to $5 \cdot 10^{-7}$ Torr, the indene radical cation was isolated by application of several SWIFT pulses and subsequently irradiated with laser light of 514.5 nm.

![Scheme 5-1. Pulse sequence applied for the determination of the cross sections $\sigma_1$ and $\sigma_2$ in the two-photon dissociation process of the indene radical cation, presented in scheme 5-3. The duration of the pulses was: quench 5 ms; electron beam ionization 130 ms; ion ejection pulses 1 and 2 to isolate the indene radical cation 8 ms and 16 ms, respectively; laser on 2000 ms; detection 5 ms. 2000 pulse sequences were accumulated to obtain spectra with and without laser light.]

A detection pulse was triggered at the end of each sequence. For details about the duration of the various pulses, see scheme 5-1. After Fourier transformation the heights of the peaks due to the indene radical cation with and without irradiation at several laser intensities and pressures of the neutral indene gas were taken as a measure of the ion abundances.

To determine the bimolecular rate constant for proton transfer from the laser-light excited indene radical cation, $k_3$, indene was introduced into the cell at a pressure of $2 \cdot 10^{-9}$ Torr together with the reference base 3-pentanone at pressures from $1 \cdot 10^{-7}$ Torr up to $6 \cdot 10^{-7}$ Torr. Scheme 5-2 gives a typical pulse sequence for the proton transfer experiments from the indene radical cation with and without irradiation. Isolation of the indene radical cations by application of repeated SWIFT pulses was followed by a relaxation period of 620 ms to carry
off the excess energy of electron ionization excited indene radical cations by nonreactive collisions (6 to 7 collisions took place). This relaxation waiting period was followed by a SWIFT ejection pulse to remove the ion/molecule reaction products formed and to isolate the “cooled” indene radical cations.

![Scheme 5-2. Pulse sequence applied for the determination of $k_4$ and $k_3$ presented in scheme 5-5. The laser pulse (depicted in dotted lines) was applied alternately on and off to obtain separated spectra. The duration of the pulses was: quench 5 ms; electron beam ionization 80 ms; ion ejection pulse 1 to remove all ions with the exception of the indene radical cations 90 ms; a waiting period to carry of excess energy of (cool) the ions 620 ms; ejection pulse 2 to isolate the indene radical cations 8 ms; ejection pulse 3 to further isolate the indene radical cations after cooling 8 ms; laser on 2000 ms; detection 4 ms. 3000 pulse sequences were accumulated to obtain the separated spectra.](image)

Finally, these ions were allowed to react for 2500 ms with the laser light on or off followed by a pulse to detect the reactant and product ions. Separate spectra with the laser light on and with the laser light off were obtained from the Fourier transformed signals of the two successive experimental cycles.

### 5.3 Background of the kinetics of the photochemical experiments

For the discussion in the next section of the results obtained, the background of the kinetics of two-photon dissociation will be given. This will be followed by the expanded kinetic model for intermolecular proton transfer from gas phase ions, such as the indene radical cation.
5.3.1 Two-photon dissociation

Two-photon photodissociation of gas phase ions has been studied since the mid seventies [33-37]. To be certain that the proton transfer occurs from excited ions, it must be shown that they obey the rules of two-photon dissociation. That is, evidence should be provided for the existence of an excited state in between the ground state and the dissociation limit of the ions. Of course, also important is the lifetime of such an excited state after internal conversion to a vibrationally excited ground state, which can be as long as 500 ms for aromatic radical cations (for more details chapter 3, chapter 6 and [29,37,38]). Scheme 5-3 presents the case for a two-photon dissociation of the ion \( M^+ \) where the symbols \( \sigma_1 \) and \( \sigma_2 \) are the cross sections for the first and second photon absorption, \( I \) the laser intensity, \( k_1 \) the rate constant for collisional deactivation, \( k_2 \) the rate constant for radiative deactivation, \( n \) the density of neutral molecules, \( M^{+*} \) the excited ion and \( F \) the generated fragments.

\[
\begin{align*}
M^+ & \xrightleftharpoons[\text{nk}_1+\text{k}_2]{\sigma_1} M^{+*} \xrightarrow{\sigma_2} F
\end{align*}
\]

Scheme 5-3. Reaction scheme for a pure two-photon dissociation process of \( M^+ \) (see further text).

To determine the ratio of the photon absorption cross sections, \( \sigma_1/\sigma_2 \), of the indene radical cation, the value of \( k_1 \) is needed. Assuming that relaxation of the excited indene radical cation in the two photon dissociation occurs purely via charge exchange with neutral indene, the collisional relaxation rate constant \( k_1 \) will be about equal to the rate constant for charge transfer from the ground state indene-d_3 radical cation to neutral indene. This system has been chosen to be able to observe experimentally the charge transfer as shown by the reaction equation in scheme 5-4.
Scheme 5-4. The reaction equation for the charge transfer from the indene-d₃ radical cation to neutral indene and vice versa.

The exact solution of the differential equation for the kinetic model in scheme 5-3 yields:

$$1-F(t) = \frac{1}{(r_1 - r_2)} \cdot (r_1 e^{-r_1 t} - r_2 e^{-r_2 t})$$  \hspace{1cm} (1)$$

where $1-F(t)$ is the fraction of the remaining indene radical cations after an irradiation time $t$ and

$$r_{1,2} = \frac{1}{2} \left\{ (I\sigma_1 + I\sigma_2 + k_2 + nk_1) \pm \sqrt{((I\sigma_1 + I\sigma_2 + k_2 + nk_1)^2 - 4I^2 \sigma_1 \sigma_2)} \right\}$$  \hspace{1cm} (2)$$

As discussed in an earlier paper [36] the following approximation is valid:

$$r_1 = (I\sigma_1 + I\sigma_2 + k_2 + nk_1)$$

$$r_2 = I^2 \sigma_1 \sigma_2 / (I\sigma_1 + I\sigma_2 + k_2 + nk_1)$$

where $r_2 << r_1$ and for times $t >> (I\sigma_1 + I\sigma_2 + k_2 + nk_1)^{-1}$ the second term in eq. 1 becomes vanishingly small. This leads to a single exponential behaviour for $1-F(t)$ from which it follows that [36]:

$$-\frac{1}{\ln\{1-F(t)\}} = (nk_1 + k_2)/(I\sigma_1 \sigma_2 t + (\sigma_1 + \sigma_2)/\sigma_1 \sigma_2 t)$$  \hspace{1cm} (3a)$$
or

\[-\frac{t^2}{\ln\{1-F(t)\}} = \frac{k_2}{\sigma_1/\sigma_2} t + \frac{l(\sigma_1+\sigma_2)/\sigma_1}{\sigma_2} t + nk_1/\sigma_1 \sigma_2 t \]

(3b)

By substituting the measured \( k_1 \) in eq. 3b, and by measuring the amount of fragment \( F(t) \) when varying the pressure and laser light intensity it is possible to calculate the ratio \( \sigma_1/\sigma_2 \) and the radiative relaxation rate \( k_2 \) using multiple regression. However, the subscripts 1 and 2 of the absorption cross sections are interchangeable in eqs. 3, so that it is not possible to assign experimentally determined values specifically to \( \sigma_1 \) or \( \sigma_2 \). Therefore, two solutions of the ratio of the absorption cross sections are possible, which are \( \sigma_1/\sigma_2 \) and \( \sigma_2/\sigma_1 \).

5.3.2 Proton transfer

Scheme 5-5 is an extension of Scheme 5-3 to include photochemical reactions of \( M^{++} \) with substrate molecules \( A \) to give the bimolecular reaction products \( P \), in which \( n_A \) is the density of molecules \( A \), \( k_4 \) the collisional relaxation constant for indene radical cations in the presence of substrate molecules \( A \) and \( k_3 \) the bimolecular rate constant for reaction of \( M^{++} \) with \( A \).

\[
\begin{align*}
M^+ & \rightleftharpoons \text{n}_A k_4 + k_2 \quad M^{++} \quad \sigma_1 \quad F \\
& \quad \text{n}_A k_3 \quad \sigma_2 \quad A \\
& \quad P
\end{align*}
\]

Scheme 5-5. Reaction scheme for a pure two-photon dissociation process of \( M^+ \), in which the singly photon excited \( M^{++} \) reacts with molecule \( A \) to give products \( P \) in competition with deactivation and absorption of a second photon to give fragments \( F \) (see further text).
From scheme 5-5 it follows that the ratio of product $P$ and fragment $F$ abundances is given by eq. 4:

$$\frac{P}{F} = n_A k_3 / \sigma_2 I$$  \hspace{1cm} (4)

The solution of the differential equation for the kinetic model in scheme 5-5 leads to eq. 5, assuming that, as in the case of two-photon dissociation at pressures in the order of $10^{-7}$ Torr [36], the radiative relaxation rate $k_2$ is much smaller than the collisional relaxation rate $n_A k_4$ and can be ignored.

$$-I(t)(1 + I \sigma_2 / n_A k_3) / \ln(1-F(t)) = (k_4 + k_3) / k_3 \sigma_1 + I / n_A (\sigma_1 + \sigma_2) / \sigma_1 k_3 \hspace{1cm} (5)$$

Thus, a plot of $-I(t)(1 + I \sigma_2 / n_A k_3) / \ln(1-F(t))$ versus $I / n_A$ at several laser intensities and several pressures of the reference base should result in a straight line with

- intercept $\phi = (k_4 + k_3) / k_3 \sigma_1 \hspace{1cm} (6)$
- slope $\varepsilon = (\sigma_1 + \sigma_2) / \sigma_1 k_3 \hspace{1cm} (7)$

From $\phi$ and $\varepsilon$ and the determined ratio of $\sigma_1 / \sigma_2$, the ratio of $k_4$ and $k_3$ can be calculated. It should be noted that, because of the ambiguity in the ratio of $\sigma_1$ and $\sigma_2$ (see above), this procedure leads to two possible values for the ratio of $k_4$ and $k_3$. 

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5.4 Results and discussion

Determination of the ratio of the relaxation rate of and the rate of proton transfer from the excited indene radical cation.

5.4.1 Charge transfer from the indene-$d_3$ radical cation to neutral indene.

As discussed in section 5.3.1 and 5.3.2, the ratio of the relaxation rate of and the rate of proton transfer from the excited indene radical cation, $k_d/k_3$, can be derived from the ratio of the cross sections for the first and second photon absorption, $\sigma_1/\sigma_2$, in the two-photon dissociation process. For the last ratio the rate constant $k_1$ is required. This rate constant $k_1$ has been obtained from the measurement of the rate constant for charge transfer from the ground state indene-$d_3$ radical cation to neutral indene, assuming that the relaxation of the excited indene radical cation occurs via this charge exchange.

Figure 5-1 shows the decay of the molecular ion of indene-$d_3$ and the rise of the molecular ion of indene as a function of time. From an exponential fit of the curves in Figure 5-1 the rate constant for charge transfer has been derived to be $7\times10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$. It should be noted that this is not an absolute value. It is, e.g., not corrected for the difference between the pressure in the ICR cell and its value read from the ionization gauge.
5.4.2 Two-photon dissociation of indene radical cations excited by laser light of 514.5 nm.

As in previous papers [29,30,36], Figure 5-2 shows $-1/\ln(1-F(t))$ versus $1/I$ for different pressures (see eq. 3a). In earlier work [36] the values of $\sigma_1/\sigma_2$ and of $k_2$ were determined from the intercept by plotting the slopes of the curves versus pressure. In the present work we used multiple regression instead (see eq. 3b). The resulting value of $\sigma_1/\sigma_2$ was 9 (or 1/9) while $k_2$ was 2 s⁻¹.

Figure 5-1. The relative abundances of the via charge exchange formed indene radical cation ($m=116$, □) and the reacting indene-d₃ radical cation ($m=119$, △) measured as function of the reaction time. The pressure used for both neutrals was $2.5\times10^{-8}$ Torr.
5.4.3 Proton transfer from the indene radical cation to 3-pentanone.

Subsequently the ratio of the rate constants for relaxation of and proton transfer from the excited indene radical cation, $k_4/k_3$, in the presence of a gas-phase neutral reference base has been determined.

To this end the laser light intensity and the pressure of the neutral reference base 3-pentanone in the presence of indene radical cations have been varied. The results are plotted as $-\ln(l + l_0/\kappa_3)/\ln(1-F(t))$ versus $l/\kappa_3$ (eq. 5) in Figure 5-3.
From the intercept and the slope of the line in Figure 5-3 the ratio \( k_4/k_3 \) has been calculated using eqs. 6 and 7 given in section 5.3.2. The results have been summarized in Table 5-1.

Table 5-1. Ratio \( k_4/k_3 \) determined from the intercept and slope of the line in Figure 5-3 and use of the determined value for \( \sigma_1/\sigma_2 \).

<table>
<thead>
<tr>
<th>( \sigma_1/\sigma_2 )</th>
<th>( k_4/k_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>1/9</td>
<td>80</td>
</tr>
</tbody>
</table>

*Because of the symmetry of the formula for the two-photon dissociation process, two values for the ratio \( \sigma_1/\sigma_2 \) are possible; see section 5.3.1*
Discussion

Although it is not clear whether the value of $k_4/k_3$ is either about 100 or about 10, it is clear that for the single photon excited indene radical cation the rate of its proton transfer to a base is considerably slower than its rate of relaxation by non-reactive collisions. Here it should be noted that scheme 5-5 is of course a simplification and that during relaxation the overall rate of proton transfer will decrease. One may therefore assume that the major part of the reaction products will be formed when the average internal energy is still relatively high. Taking a CH stretching frequency of 3000 cm$^{-1}$, the observed 0.5-0.6 eV energy available for the endothermic proton transfer corresponds with 1.5 vibrational quanta in the relevant CH-bond. Assuming energy randomization, this does not seem unreasonable for the possibility of reaction. Because prior to energy randomization internal conversion to a highly vibrationally excited ground state has to occur, it is important to measure the quantum yields for fluorescent and phosphorescent relaxation of the single photon excited indene radical cation to estimate the amount of internal conversion.

5.5 Conclusions

In chapter 3 of this thesis it has been shown possible to determine the threshold for proton transfer from laser-light excited protonated naphthalene to a base in the gas phase by use of the bracketing method as applied in our previous study to the laser-light excited indene radical cation in chapter 4 of this thesis and ref. 30. For protonated naphthalene excited by light of 488 nm (2.54 eV) it has been found in this way that the proton transfer to a base can be as endoergic as 60 kJ/mol. This value is very similar to that for the radical cation of indene excited by light of 514.5 nm (2.41 eV) where the proton transfer to a base can be as endoergic as 48 kJ/mol. The observed 0.5-0.6 eV energy available for proton
transfer to a base seems reasonable when taking into account a complete randomization of the initially deposited energy in the ions. In the next chapter, the epilogue, a more elaborate discussion is presented on the experimentally obtained results described in the previous chapters.
References


