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Femtochemistry of the iodine–arene charge-transfer complex

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Femtosecond spectroscopy is used to investigate the ultrafast photochemistry of the I_2:arene charge-transfer complex that occurs upon excitation into the charge-transfer state. We find that the photo-excited complex branches into two different channels within 25 fs. The dominant channel involves breaking up of the I_2:arene complex in its constituent molecules, in the other channel the I:arene complex and an iodine atom are formed. From the polarization anisotropy and the absence of fast geminate recombination of the I:arene and atomic iodine fragments we conclude that in the transition state the I_2:arene complex is severely distorted. The molecular I_2 formed in a separate channel of the reaction recombines with arene to I_2:ar in about 10 ps.

1. Introduction

With the advent of femtosecond lasers [1], new opportunities arose for the study of the elementary steps in chemical reactions. The promise of this new field named "femtochemistry" was most vividly demonstrated by Zewail and co-workers [2]. It was shown that the dynamics of the initially excited state of the reactant can be expressed elegantly in terms of the time evolution of a wave packet [3,4]. In certain reactions this time evolution leads to products that are formed in a coherent superposition of rotationally and/or vibrationally states [5], which can be described by wave packets as well. For instance, in case of the photodissociation of HgI_2 it was shown that the HgI photofragment is generated as a *ro-vibrational* wave packet [6]. For ICN it has been predicted that the CN fragment is formed as a *rotational* wave packet [7], with little energy going into vibrational excitation of the photoproduct. Recently it was demonstrated that photodissociation of I_3^- in solution leads also to one of the fragments (I_2^-) being formed as a vibrational wave packet [8]. It can be expected that the course of this reaction, and any other that occurs in solution, is greatly influenced by the collisional dynamics of the solvent [9]. Study of these dynamics is therefore crucial to the understanding of the effect of vibrational coherence on chemical reactions in solution. Recently femtosecond four-wave mixing [10,11] and optical Kerr effect [12] experiments have been performed to study the ultrafast solvent dynamics. While substantial progress is being made in the understanding of the different types of solvent motions, their effect on the product coherence has not been explored. Understanding of these effects remains one of the main challenges in this field.

In this Letter, we report on the ultrafast photochemistry of a simple charge-transfer complex in solution: the iodine–arene (I_2:ar) complex. This system played an important role in Mulliken's theoretical description of charge-transfer complexes [13]. The reasons for our choice of this complex are rather basic: (1) it seemed an excellent model system to study the role of solvent motion on a reaction, (2) the photodissociation reaction involves only breaking of a *single* iodine–iodine bond [14] (vide infra), (3) there seemed to be a fair chance that a vibrationally coherent product would be formed in the reaction. Moreover, the absorption spectra of these complexes have been characterized well [15–17] and extensive ps pump–probe studies of this reaction were already performed [18,19]. In fact our femtosecond pump–probe study can be considered a follow up of these pioneering ps experiments, which established clearly the very fast formation of the I:ar

complex. However, due to limited time resolution in these earlier studies the elementary step in the photodissociation of the I_2:ar complex could not be observed. In particular the question whether or not branching occurs in this reaction could not be settled. Unravelling the photodissociation of an iodine complex is also appealing because iodine has always played a prime role in the study of reaction dynamics in solution (for a review, see ref. [20]). Fundamental processes such as predissociation and curve crossing [21], geminate recombination and the cage effect [22], and vibrational relaxation [23] have all been explored in this system.

We find that dissociation of iodine in the I_2:ar complex, by excitation into the charge-transfer band, proceeds much faster than in the B state of free molecular iodine [24] and that the I:ar photoproduct is not formed in a coherent-wavepacket state. Clear evidence for the concurrent generation of molecular iodine from the I_2:ar complex in a separate channel is also presented. A model for the reaction is proposed that accounts for the absence of fast geminate recombination and for the ultrafast loss of polarization anisotropy. Recombination of molecular iodine and arene molecules is found to be complete in about 20 ps, while this process for the I:ar and atomic iodine fragments occurs only partly and takes place on a much longer time scale.

2. Experimental

The experimental setup used is similar to the one described previously [25]. Pulses of 2 μJ with a duration of about 50 fs were generated in a CPM laser amplified by a copper vapor laser. Pump and probe beams at 310 nm were obtained by second harmonic generation in a 300 μm thick KDP crystal. The UV light is generated with a polarization perpendicular to the red light. In some pump–probe experiments the polarization of the probe beam at 620 nm was rotated over 90° by placing a $\frac{1}{2}\lambda$ plate in the beam. Probe beams in other parts of the spectrum were obtained by continuum generation in a thick (about 1 mm) flowing jet of ethylene glycol. Portions of this continuum were selected by placing interference filters, with a bandpass width of about 25 nm, between the sample jet and the detector. In this manner probe wavelengths from 700 down to 400 nm, at 50 nm in-

tervals, could routinely be obtained. Cross correlation widths of this pump–probe setup were typically about 140 and 120 fs for the single-colour and the two-colour configuration, respectively.

Samples were prepared by dissolving solid, triply sublimed, iodine (Merck) either in pure mesitylene (1,3,5-trimethylbenzene) or toluene, or in 20/80 vol% mixtures of mesitylene/toluene and alkane (n-hexane, cyclohexane, n-hexadecane). The concentration of iodine in all cases was about 5×10^{-3} M. In the pure arene solvents the equilibrium $I_2 + ar \rightleftarrows I_2$:ar is such that about 85% of the iodine is complexed in case of mesitylene and about 70% for toluene. For the mixed solution samples (20% vol. conc.), about 60% of the iodine is complexed for alkane/mesitylene, while for alkane/toluene this fraction is 45%, as established by inspection of the intensity of the charge-transfer transition. All solvents were Merck p.a. grade and used as provided by the manufacturer.

3. Results and discussion

Fig. 1 shows the spectrum of iodine dissolved in mesitylene. The band around 490 nm is also present when iodine is dissolved in inert solvents, such as cyclohexane, although in complexing solvents it is somewhat shifted to the blue. The band with a maximum at 334 nm, on the other hand, is not present in either mesitylene or iodine; it belongs specifically
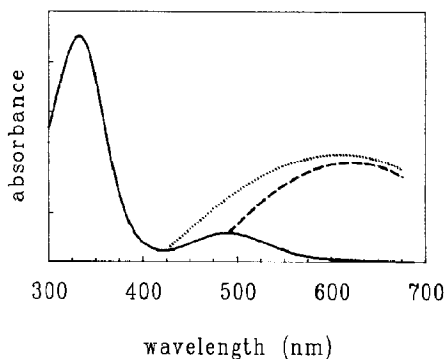

Fig. 1. (——) Absorption spectrum of a solution of I_2 in mesitylene. In the same figure, on an arbitrary scale, sketches of the transient absorption spectra measured at (···) 1 ps and (– – –) 30 ps probe delays (dashed line).

to the charge-transfer complex I_2:mes. The spectrum of iodine in toluene is very similar except that the charge-transfer band is now found at 300 nm. The transient absorption spectra of the photoproduct [14,16] have also been reported but using ps pump and probe pulses [19]. The transient spectra measured after fs excitation are more informative and shown in fig. 1. The dashed curve presents the spectrum obtained at a probe delay of about 30 ps. This spectrum is dominated by the well-known absorption of the I:mes photoproduct. The dotted curve in fig. 1 presents the transient spectrum obtained at a probe delay of 1 ps. By comparing the "late" and "early" spectra it is clear that the "early" transient absorption spectrum exhibits a marked additional absorption on the blue side of the I:mes spectrum. For the I_2:tol complex similar transient spectra were obtained but the I:tol photoproduct absorption maximum is now found to be located at 500 nm.

To further unravel the reaction path of the I_2:arene complex the system was excited in its charge transfer band using an 80 fs pump pulse, while the photoproduct absorption was probed with a high time resolution over the wavelength range from 400 to 700 nm. The measured fs and ps transients expose essentially the same features for iodine dissolved in the pure arenes or mixed arene/alkane solutions. Fig. 2 displays the short time behaviour of the dual colour (310 nm/620 nm) pump–probe transient for the I_2:mes complex in pure mesitylene. It shows that the absorption signal rises instantaneously with the pump pulse. As the signal exhibits its maximum absorption around 600 nm it has the spectral characteristics of the iodine atom–mes (I:mes) complex, as previously reported by Hilinski and Rentzepis [19]. Fig. 2 further shows that after this instrument-limited response the signal climbs in 400 fs to its maximum intensity. At this level it remains stationary for a few picoseconds and then decays slowly on a time scale of hundreds of picoseconds. Basically the same spectral dynamics was observed for the I_2:tol complex. The immediate conclusion from these experiments is that the excited I_2:ar charge-transfer complex undergoes ultrafast dissociation into an iodine atom and an I:ar complex. In the earlier picosecond pump–probe experiments this elementary event could not be observed [19]. Our time resolution poses an upper limit of 25 fs to the time it takes to break the io-
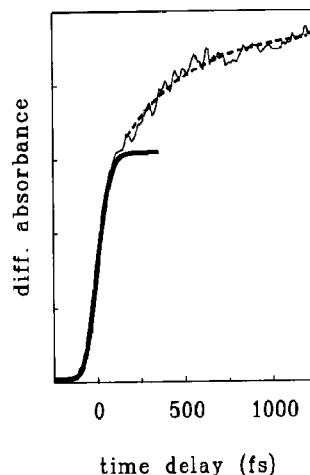

Fig. 2. Short-time behaviour of the pump–probe signal in I_2/mesitylene. Pump wavelength 310 nm, probe wavelength 620 nm; the probe is polarized parallel to the pump pulse. The system response function, obtained by integrating the sum-frequency signal in KDP measured in the same setup, is given by the heavy line. The dashed line is a fit to the data using a time constant of 400 fs.

dine–iodine bond in the I_2:ar complex. This leads us to suggest that the fragmentation process proceeds on a repulsive excited state potential. The subsequent increase in signal intensity on a sub-picosecond time scale is assigned to the formation of additional I:ar complexes. These are formed by I atoms that are launched into the solvent and subsequently react with other arene molecules. Strong support for this interpretation is provided by our findings that the amplitude of the 400 fs transient is about the same as the ultrafast one in mesitylene, while it is much less intense in mixed arene/alkane solutions. The *formation* of secondary I:ar complexes from its separate constituents is thus a fast process (400 fs), although the I:ar bond is rather weak compared to a regular covalent chemical bond.

The early spectral evolution of the photoproduct, depicted by the dotted curve in fig. 1, hints at the formation of another species in the reaction that absorbs around 490 nm. Hilinski and Rentzepis [19] assigned this absorption to the positively charged mesitylene radical of the I_2^-:mes$^+$ charge-transfer complex, which they suggested to be the first product in the reaction. The transient spectrum of I_2^-, however, was not observed. Their analysis of the spec-

trum at early times was also severely hampered by the fact that they were using ps excitation and probe pulses. When our transient absorption spectra at probe delays of 1 and 30 ps are compared, it is evident that the early "blue" spectrum shows a striking similarity with the molecular iodine spectrum. We therefore conclude that the "blue" transient is due to molecular iodine created by impulsive fragmentation of the I_2:mes complex rather than to the positively charged mesitylene radical. Our experiments also show that both photoproducts: the $I_2 + ar$ and I:ar+atomic I fragments are formed on the same time scale, suggesting that they exit from parallel routes.

To further probe the slow dynamics of the products we performed single and dual colour pump–probe experiments on the spectral evolution of the excited I_2:mes complex for probe delays up to 100 ps. In all cases the excitation wavelength was 310 nm. The lower trace in fig. 3 shows that at the excitation wavelength (310 nm) a substantial recovery of the absorption takes place with a time constant of 13 ± 2 ps. On the same time scale the "blue" transient was also found to disappear. The major reaction channel (about 75%) therefore involves expulsion of the iodine molecule from I_2:mes, but the original I_2:mes
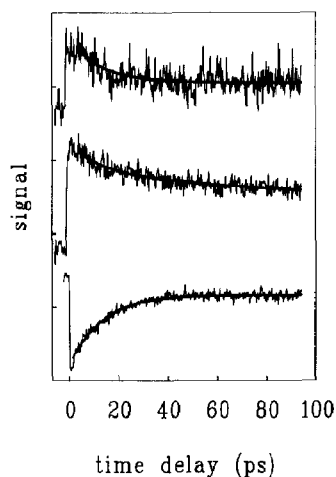

Fig. 3. Pump–probe transients for I_2:mes in mesitylene. Increased absorption is shown as a positive signal, while increased transmission is presented as a negative one. In all cases the pump wavelength is 310 nm. The probe wavelengths are 500 nm (upper trace), 600 nm (middle trace) and 310 nm (lower trace), respectively.

complex is almost completely regenerated on a time scale of 10 ps. The upper and middle traces in fig. 3 present the spectral evolution at probe wavelengths of 500 and 600 nm, where the absorption spectrum is dominated by the I:mes complex. The first thing to note is that the overall decay of these transients is much slower and furthermore that the absorption recovery is far less pronounced than for the UV probe. These decays are also clearly bi-exponential with time constants of 13 and 150 ps. Furthermore the relative amplitude of the fast decay is found to increase with decreasing wavelengths, indicating that the fast and slow decays are due to the decay of different species.

These findings corroborate the earlier suggestion [19] that photodissociation of I_2:ar leads to the formation of two different photoproducts, which exhibit different dynamics. In this reaction scheme the 13 ps decay component in the transients is due to recombination of molecular iodine and mesitylene. Since the same time constant is observed for the 20%/80% diluted solutions, it is dominantly geminate recombination that occurs. The 150 ps decay components, most likely, results from the combined effects of vibrational cooling, recombination of the I:mes and atomic I fragments to the original complex and, possibly, a chemical reaction of the I:mes complex. Indeed, it is known that the I:mes complex can react to iodo–mesitylene [26]. This analysis of the slow spectral dynamics gains further weight from the fact that I_2:tol shows similar dynamical behaviour but with the molecular–iodine producing channel being less efficient (about 70%). Also its transient spectrum exhibits a less pronounced slow decay component, in agreement with the known higher chemical stability of I:tol compared to I:mes [26]. The slow decay component for I_2:tol may also be reduced, because in toluene our excitation wavelength lies at the top of the band, whereas in mesitylene, we excite in the blue flank. The photoproduct I:tol is therefore expected to be formed with less excess vibrational energy, and vibrational cooling effects will thus be less important than for I:mes.

Noteworthy is also the fact that in fig. 3 no indication of fast geminate recombination is noticeable for the I:mes and free I atom products. As electron donors are known to catalyze the recombination process of free iodine atoms [27] a rather strong "cage

effect" was expected. Its absence here is surprising, especially in the light of recent work by Harris and co-workers [28], who found that fast single-collision geminate recombination is a ubiquitous feature in bond-breaking reactions. The lack of a cage effect in this bond-breaking reaction should therefore bear directly on the mechanism of the dissociation process itself.

In the remainder of this Letter, we will mainly discuss the fate of the I:ar photoproduct. The reason is that the other product, molecular iodine, has not been studied in the same detail yet. An important piece of information on the early dynamics along the reaction path is provided by a measurement of the polarization anisotropy, which is defined as

$$\rho \equiv (S_\| - S_\perp)/(S_\| + 2S_\perp) , \qquad (1)$$

where $S_\|$ and $S_\perp$ represent the intensity of the pump–probe signals obtained with parallel and perpendicular polarizations, respectively.

For the I_2:mes in mesitylene the measured anisotropy is presented in fig. 4 for the 310 nm/620 nm pump–probe combination, which is dominated by the response of the I:mes photoproduct. Noteworthy is the initial low value (0.1) of the polarization anisotropy (ρ). Also is shown that the polarization anisotropy decays ultrafast, with time constants of about 320 fs and 1.5 ps. The very rapid decay is clearly too fast for diffusive rotational motion, especially in a liquid such as mesitylene, where strong intermolecular interactions occur. Some kind
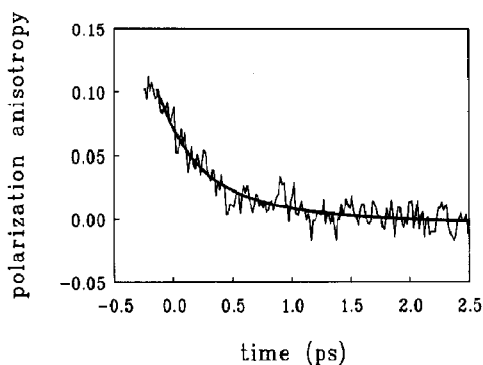

Fig. 4. Plot of the polarization anisotropy of the 620 nm probe signal after excitation at 310 nm in the I_2:mes complex. The heavy line represents a biexponential fit with time constants 320 fs and 1.5 ps.

of *forced* ultrafast rotational motion seems to be taking place.

Prior to presenting a specific model for the dissociation process, let us first review briefly what is known about the structure of the I_2:ar and I:ar complexes. From a study of the IR absorption spectrum of I_2:ar in a low-temperature argon matrix [17] and theoretical calculations [29] it was inferred that I_2 assumes an axial position in the I_2:ar complex. A similar study of the I:ar complex showed that also here the iodine atom is positioned above the center of the arene ring [17]. The dipole moment of the ultraviolet CT transition of I_2:ar as well as of the visible CT transition of I:ar will therefore be perpendicular to the arene ring.

When the transition dipole moments of the reactant and product absorptions make an angle θ with one another, it can be shown that for the polarization anisotropy the following relation holds [30]:

$$\rho = \tfrac{3}{5}\cos^2\theta - \tfrac{1}{5} . \qquad (2)$$

Substitution of the experimentally observed value of $\rho = 0.1$ yields $\theta = 45°$. Such a value of θ can only be reconciled with the above data if the photoproduct is formed from an initially severely distorted conformation of the I_2:ar complex. This implies that, after excitation in the charge–transfer band, there is very rapid dynamics along the I–I–ar bending mode.

From the above considerations the photodissociation of I_2:ar can be envisioned to occur as shown in fig. 5. On optical excitation the complex proceeds ultrafast to a severely distorted transition state, which, in the next step, fragments into either molecular iodine and arene or into an I atom and an I:ar complex. While this reaction scheme is best looked at as an "artist's impression", its appeal lies in the fact that it explains the ultrafast loss of polarization anisotropy in a natural way. The first step along the reaction path distortion of the complex and the concomitant breaking of the iodine–iodine bond, leads to the low initial value (0.1) of polarization anisotropy ρ; the next step, impulsive rotation of the I:ar fragment by the torque created in the dissociation, yields an additional fast component in ρ (320 fs decay); and, finally, diffusive motion of the fragments is responsible for the ps decay of ρ.

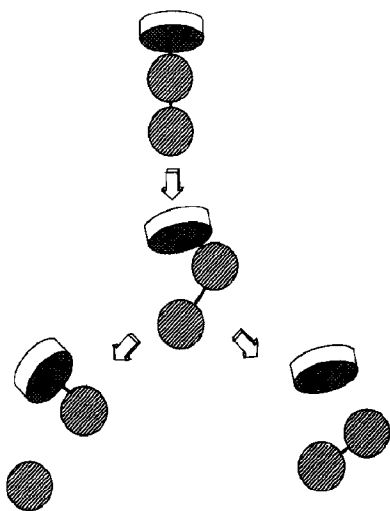An educated guess about the energy that is initially deposited in the rotational motion of the fragment

Fig. 5. Artist's impression of the model for the dissociation of the I_2:ar complex. The balls denote I atoms, the disk represents an arene molecule. Upper drawing: the equilibrium configuration of the I_2:ar complex; middle one: the transition state in the dissociation process; lower drawing: the situation immediately following iodine–iodine or iodine–arene bond ruptures.

can be made by using a model that was developed to describe dephasing of a rotational wavepacket in a gas-phase molecule [7]. According to this model, the average rotational energy (in cm^{-1}) is

$$\langle E_R \rangle \approx 4.8/B\tau^2 , \qquad (3)$$

where B is the rotational constant of the fragment (in cm^{-1}) and τ is the dephasing time (in ps) of the rotational wavepacket. By equating τ with the observed depolarization time constant of 320 fs and by taking $B = 0.02$ cm^{-1} for the rotational constant of the I:ar fragment we calculate $\langle E_R \rangle = 2340$ cm^{-1}. The initial rotational temperature of the I:ar fragment is thus estimated to be 3370 K; a very hot photoproduct indeed. Note that application of eq. (3) is warranted only when the rotational motion of the photoproduct is inertial.

The presented model for the reaction accounts also for the absence of fast geminate recombination of the I:ar and iodine atom fragments. Due to a forced rotation of the I:ar fragment, the products are not able, before escaping from the solvent cage, to regain the proper position for a reunion. The fact that virtually complete recombination of molecular iodine and arene is observed suggests that expulsion of the iodine

fragment from the I_2:ar complex occurs earlier along the reaction path.

As stated in section 1 one of the reasons why we chose the I_2:ar complex was our hope that the I:ar fragment would be formed in a vibrational coherent state [5,6,8]. A prime candidate for this effect seemed the I↔ar vibration. In our studies of the photochemistry of the I_2:ar system, we have found, however, no evidence for the coherent excitation of any vibrational mode. This can be explained very well with our model for the dissociation process in which most of the excess energy in the reaction is deposited in the *rotational* motion of the I:ar fragment. Subsequently, vibrational heating of this librating fragment may occur due to collisions with molecules in the first solvation shell. As this is a *stochastic* process it will not lead to coherent excitation of a vibrational mode. The proposed reaction scheme obviously needs further testing, both by additional experiments and by calculations. Spectroscopic experiments on the I_2:ar complex in a supersonic expansion especially should be highly informative. Our model predicts that in the gas phase the I_2 and I:ar fragments will be rotationally hot. Previously this effect has been demonstrated in case of the photodissociation reaction of ICN where the CN fragment is generated as a rotationally hot species [31].

We end by reporting on a fast transient observed in many of the dual-colour pump–probe experiments, especially on mixed solutions of I_2:ar in alkanes. This feature can be simulated by a convolution of the pump–probe correlation with an exponential decay of 150 fs. Its intensity depends on the kind of arene as well as on the dilution. It is most intense for the alkane/arene solutions, somewhat less for the toluene solution, and not discernible for the mesitylene solution. These observations, together with the spectral characteristics of the transient, suggest that it is due to uncomplexed iodine present in the solution. This idea was confirmed by our observation of the same transient in a solution of iodine in pure cyclohexane. This transient is therefore not relevant to the excited state dynamics of the I_2:ar complex and was therefore not further discussed here.

4. Summary and conclusions

We have shown that the photodissociation reac-

tion of the I_2:arene charge-transfer complex proceeds via two channels. The dominant one involves expulsion of molecular iodine, in the other channel the iodine–iodine bond is broken. Both bond-breaking reactions occur within 25 fs and are therefore assumed to take place on a repulsive excited state potential. After dissociation fast recombination occurs for molecular I_2 and arene, but recombination is a slow and minor event in case of the I:ar and atomic I fragments. To explain the fast loss of polarization anisotropy it is suggested that the transition state of the I_2:ar complex is severely bent. Future work will be directed at determining the branching ratio for excitation into the molecular-iodine-like states of the I_2:ar complex. Molecular beam spectroscopic studies of the I_2:ar complex are also called for to further elucidate the course of this important prototype reaction.

Acknowledgement

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