Picosecond Photochemistry of I_2–Arene Complexes

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Abstract: Solutions of I_2 in benzene, toluene, and mesitylene were excited at 532 nm and studied by means of picosecond absorption spectroscopy. An identical series of spectra were recorded for each solution at selected times after excitation at 355 nm, a wavelength that lies within the charge-transfer absorption band of the I_2–arene electron donor–acceptor complex. Time-dependent changes of the transient absorption spectra recorded at times from 0 to ~25 ps after excitation imply the formation of the radical-ion pair $[AR^{+}\cdot,I_2^{-}\cdot]$ either as an intermediate formed prior to the formation of the I–arene complex or as an intermediate in a reaction that occurs concurrently with the direct dissociation of the I_2–arene complex into two I atoms which rapidly complex with arene solvent molecules.

1. Introduction

In 1949, Benesi and Hildebrand[1] wrote that "the various colors of iodine in different solvents have attracted the attention of investigators for over half a century". Thirty-six years later, the photophysics and photochemistry of I_2 in condensed media continue to be the focus of a number of research endeavors.[2-6] The results of our study reported here pertain to the photochemistry of I_2 in benzene (BEN), toluene (TOL), and mesitylene (MES).

Solutions of I_2 in a variety of arenes (AR) have been studied by means of electronic absorption spectroscopy.[1] These solutions exhibit hypsochromic shifts of the I_2 visible absorption band maximum that is observed for I_2 in carbon tetrachloride or saturated hydrocarbons. In addition, these arene solutions exhibit a new absorption band in the near-ultraviolet. The absorption spectra of I_2–arene solutions have been interpreted in terms of electron donor–acceptor complex formation as described within the context of Mulliken's charge-transfer theory.[7] In particular, the UV absorption band is assigned to an AR → I_2 charge-transfer transition. In their studies of I_2–arene solutions, Benesi and Hildebrand found that ~60 % of the I_2 in pure benzene is present as a weakly bound, 1:1 I_2–benzene complex and that, in neat mesitylene, 85 mol % of the I_2 is bound to mesitylene.

Flash photolysis of I_2–arene solutions in the microsecond time regime generates transient visible absorption bands which have been assigned to iodine atom–arene complexes.[8-10] Using a mode-locked Nd:glass laser system with sample excitation at 530 nm, Eisenthal and co-workers[6] studied the formation kinetics of I-benzene and I-mesitylene complexes by measuring absorbance changes at 530 and 627 nm, respectively. In their investigations, they found that (1) photodissociation of I_2 is not affected by the fact that I_2 is weakly bound to an aromatic molecule, (2) the reaction between the iodine atom and the arene to form the new I-arene complex occurs in less than 10^{-11} s and effectively competes with the I atom cage recombination effect in neat aromatic solvents, and 3) a cage effect involving I atom recombination with an I–AR complex is small but observable in benzene but not in the I atom complexes with *p*-xylene or mesitylene.

Our studies of I_2–arene complexes provide picosecond absorption data for wavelengths ranging from 360 to 835 nm. An analysis of the time-dependent changes associated with transient absorption spectra recorded at selected times after excitation of I_2–arene solutions at either 532 or 355 nm indicates that the radical ion pair $[AR^{+}\cdot,I_2^{-}\cdot]$ is an intermediate in the formation of the I–arene complex or lies along a parallel path for the production of the I–arene complex in addition to a direct photodissociation of I_2 in arene solutions to give I–arene.

2. Experimental Section

The solvents, benzene, and toluene (MCB, OMNISOLV) and mesitylene (Aldrich, 99%) were used as received. Iodine used in these experiments was reagent grade (J. T. Baker) and was used without further purification.

The picosecond absorption experimental apparatus used in this study has been described previously.[11] It consists of a passively mode-locked Nd^{3+}:YAG oscillator which generates a train of 25-ps fwhm 1064-nm pulses. A single pulse is selected by means of a Pockels cell and crossed polarizers. This single pulse is amplified by two Nd^{3+}:YAG amplifiers and passed through a KDP crystal to generate 532-nm light. When necessary, a 355-nm excitation pulse can be generated by passing the 532-nm pulse and the residual 1064-nm pulse through a third-harmonic-generating crystal. Excitation pulse energies are ~1.0–1.5 mJ per pulse. The sample can be interrogated over wavelengths ranging from ~400 to 835 nm by means of a 25-ps continuum pulse which is generated when the sufficiently energetic, residual 1064-nm pulse is focused through a cell containing a mixture of D_2O and H_2O. This continuum pulse is split into the sample and reference pulses before reaching the sample and reference cells. Both continuum pulses are focused onto the slit of a 0.25-m spectrograph whose output is imaged onto a PAR ISIT vidicon coupled to a PAR 1216/1215 OMAA2 system that is interfaced to a Data General Eclipse S/130 minicomputer. The laser system was operated in gated-free-run mode at ~1.5 pulses per second. Each difference absorption spectrum is the result of at least 90 no-excitation/excitation pairs of laser shots. To record transient absorption spectra to wavelengths as short as ~315 nm, the continuum pulse is generated by focusing a sufficiently energetic 532-nm pulse into the D_2O/H_2O cell. This 532-nm pulse is itself generated by passing the residual 1064-nm pulse through a third Nd^{3+}:YAG amplifier and a second-harmonic-generating crystal. This time-resolved absorption measurement system incorporates UV-transmitting continuum direction and collection achromatic optics as well as a UV scintillator on the ISIT detector face.

The sample and reference cells for these experiments were 2 mm optical path length quartz cells. Solutions of 1.0–3.5 mM iodine in either benzene, toluene, or mesitylene were prepared. The electronic absorption spectra of the I_2–BEN, I_2–TOL, and I_2–MES samples were recorded with a Cary 15 spectrophotometer before and after the time-resolved laser experiments. Neither the number of excitation shots nor the history of the samples used was found to have influence in the observed ground-state or transient-state absorption spectra.

3. Results and Discussion

When a solution of I_2 in benzene is excited at either 532 or 355 nm, an essentially identical series of time-resolved difference

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[†] Florida State University.
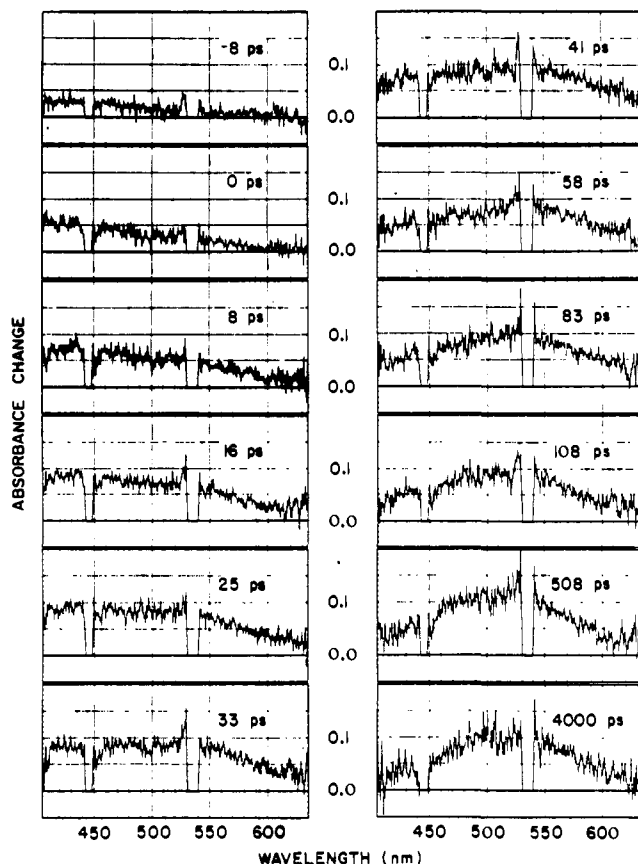* Address correspondence to this author at AT&T Bell Laboratories.

Figure 1. Difference absorption spectra recorded at selected times after 532-nm excitation of a 1.7 mM I_2 solution in benzene. The spectral regions near 532 and 455 nm are obscured as a result of a filter used to reject the scattered 532-nm excitation light.
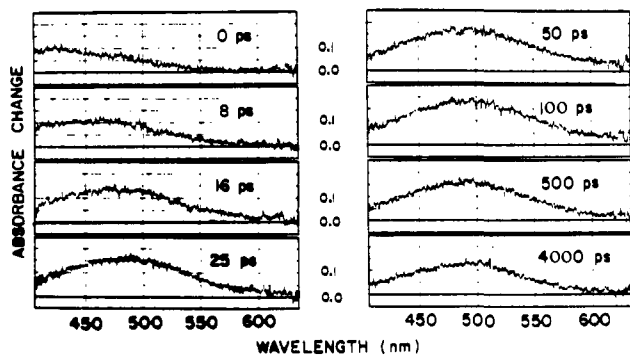

Figure 2. Difference absorption spectra recorded at selected times after 355-nm excitation of a 1.8 mM I_2 solution in benzene.

absorption spectra result. These spectra are illustrated in Figures 1 and 2. For either excitation wavelength at 0 ps after excitation, which is on the rising edge of the excitation and interrogation pulses, the difference absorption spectum exhibits a λ_{max} at ~425 nm. This λ_{max}[19] is shifting during the 25 ps of the laser pulse

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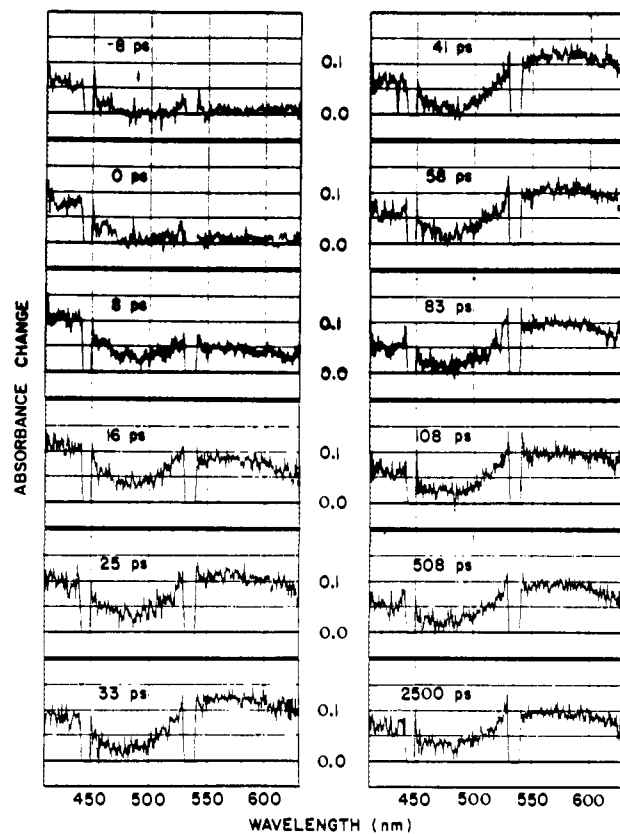(19) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632

Figure 3. Difference absorption spectra recorded at selected times after 532-nm excitation of a 1.8 mM I_2 solution in mesitylene.
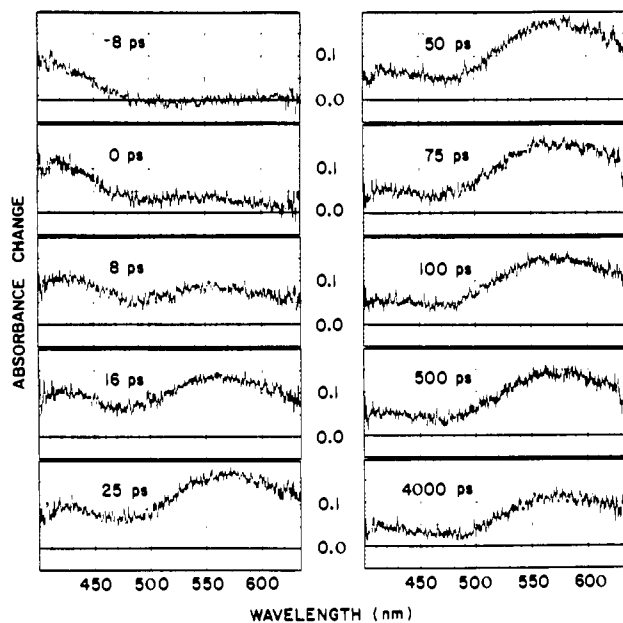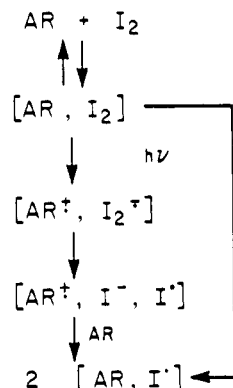

Figure 4. Difference absorption spectra recorded at selected times after 355-nm excitation of a 1.1 mM I_2 solution in mesitylene.

duration. For times > 25 ps after excitation, λ_{max} changes to 495 nm which is the equilibrium λ_{max} reported for the I–BEN complex.[9] The major cause of this bathochromic shift of λ_{max} is group velocity dispersion which is ~8 ps for 575 nm relative to 450 nm; i.e., within a given spectrum recorded at a particular delay time, ΔA at 450 nm actually is recorded ~8 ps before ΔA at 575 nm. Once the formation of the I–arene complex is complete and certainly for times < 500 ps after excitation, the absorption band intensity remains unchanged. During early times prior to stabilization of λ_{max} at 495 nm, close inspection of the intensity at ~415 nm reveals that it is changing slightly with increasing time.

Scheme I

$$AR \; + \; I_2$$

$$[AR \, , \, I_2]$$

$$\downarrow h\nu$$

$$[AR^{\ddagger}, \; I_2^{\ddagger}]$$

$$[AR^{+}, \; I^{-}, \; I^{\bullet}]$$

$$\downarrow AR$$

$$2 \; [AR, I^{\bullet}]$$

In Figure 1, $\Delta A_{415} \cong 0.095$ between 0 and 8 ps after excitation. ΔA_{415} then begins to decrease with time until a constant value of $\Delta A_{415} \cong 0.075$ is achieved between 25 and 500 ps after excitation, the time regime within which $\lambda_{max} = 495$ nm is stable. In these experiments, there appears to be no significant amount of I–I· recombination occurring between two I–BEN nearest neighbors. If the shift of λ_{max} with time was the result only of group velocity dispersion, then absorbance changes at wavelengths starting from blue to red should grow to their maximum values during the time duration of the laser pulse and remain there for at least ~500 ps. Because this is not the case, there appears to be some intermediate or concurrent process occurring during the time of formation of the I–benzene complex.

Figures 3 and 4 illustrate the transient absorption spectra exhibited by solutions of I_2 in mesitylene that are excited at 532 and 355 nm, respectively, and interrogated at selected times after excitation. It is noted that irradiation of I_2 in mesitylene leads to consumption of I_2,[9] but the decrease in I_2 concentration was not significant during the course of a time-resolved laser absorption measurement as described here. As in the case for excitation of I_2–benzene solutions, a similar absorption band for I_2–MES solution with a maximum at ~580 nm is observed which reaches its maximum intensity within the 25-ps pulse duration and remains unchanged in intensity to times of ~500 ps after excitation. We assign this 580-nm band to the I–mesitylene complex.[9] The ΔA intensity changes near 420 nm which occur within the time duration of the laser pulse are more obvious for I_2–MES solutions than for I_2–BEN solutions. In Figure 3, ΔA_{420} has reached its maximum of ~0.1 in the spectrum labeled 8 ps. By ~50 ps after excitation, ΔA_{420} has decreased to ~0.06. While the apparent lag in the growth of the 480-nm wavelength maximum is in part due to group velocity dispersion within the interrogation pulse, the time-dependent ΔA_{420} intensity clearly indicates the existence of an intermediate step or parallel path involved in the photochemistry of I_2–MES.

Similar time-dependent behavior is illustrated in Figure 5 for excitation of I_2 in toluene at 532 nm. The broad absorption band with a maximum near 510 nm is assigned to the I–TOL complex.[9]

From these data, it is clear that some intermediate step prior to I–arene complex formation or a process occurring concurrently with formation of the I–arene complex exists when solutions of I_2 in arenes are excited at either 532 or 355 nm. Indeed, excitation at 532 nm leads to the same series of transient absorption spectra as does excitation at 355 nm. Based on the data presented, we propose the mechanism outlined in Scheme I.

From the work of Benesi and Hildebrand,[1] it is known that an I_2 solution in benzene, toluene, or mesitylene exhibits a visible band maximum at 500, 497, or 490 nm, respectively, which is hypsochromically shifted relative to the absorption band maximum at 517 nm which is exhibited by solutions of I_2 in carbon tetrachloride. The absorbance at λ_{max} is nearly the same for equal concentrations of I_2 in benzene, toluene, mesitylene, *and* carbon tetrachloride. In a neat benzene solution of I_2 at room temperature, ~60 mol % of I_2 exists in the form of an I_2–BEN complex, and in a mesitylene solution of I_2, 85 mol % of the I_2 is bound to mesitylene. For I_2 in toluene, the amount of I_2 complexed with
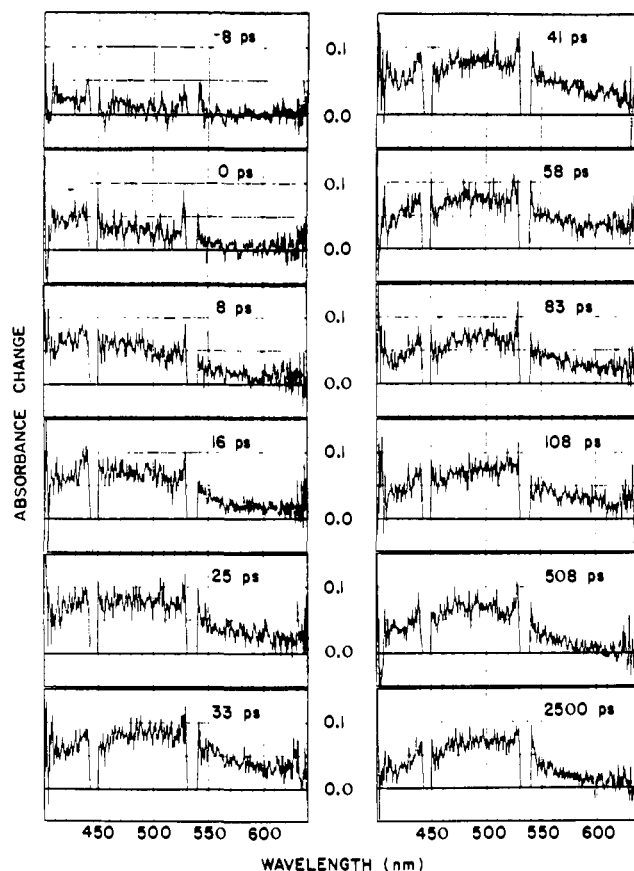

Figure 5. Difference absorption spectra recorded at selected times after 532-nm excitation of a 2.0 mM I_2 solution in toluene.

toluene should be between 60 and 85 mol %. These facts indicate that a significant amount of the visible absorption band intensity is due to the I_2–arene complex.

The UV absorption band which is exhibited by ground-state I_2–arene solutions has been assigned to an AR → I_2 charge-transfer (CT) transition.[1,7] The absorption maximum of this CT band is observed at 297, 306, and 333 nm for I_2 solutions in benzene, toluene, and mesitylene, respectively. On the basis of results that we have obtained[12,13] for excitation of other electron donor–acceptor (EDA) complexes, specifically at wavelengths within the CT absorption bands of the EDA complexes and excluding any direct excitation of either the donor or acceptor component, it is expected that excitation of the I_2–arene EDA complex at 355 nm will generate, within the time duration of the excitation pulse, the radical-ion pair $[AR^{+\cdot}, I_2^{-\cdot}]$ in solution. This radical-ion pair has been postulated as an intermediate in the photochemical iodination of aromatic hydrocarbons.[14]

Excitation at wavelengths corresponding to primarily a donor absorption band or primarily an acceptor band and not a CT band exclusively associated with an EDA complex may lead to a number of additional photophysical and photochemical phenomena associated with EDA complexes besides radical-ion pair formation.[15] However, the time-resolved absorption spectra recorded after 532-nm excitation of the I_2–arene solutions reveal time-dependent changes that are identical with those observed for excitation at 355 nm.

As previously noted, it is difficult to assess quantitatively the photochemical conversion of I_2 in arene solution to the I–arene complex.[8–10] One should note that the series of difference absorption spectra shown in Figures 1–5 are composed of the superposition of at least two absorption bands. These are a negative absorption band, resulting from depletion of the original ground-state population, and a positive absorption band, resulting from generation of two I–arene complexes per I_2 molecule.

If the radical-ion pair $[AR^{+\cdot}, I_2^{-\cdot}]$ is generated in a step prior to formation of the I–arene complex or concurrently with direct

formation of the I–arene complex from I_2 and the $[Ar^+\cdot,I_2^-\cdot]$ lifetime is greater than ~10 ps, the absorption spectra of $I^{2-}\cdot$ and $AR^+\cdot$, in principle, should appear in the time-resolved absorption spectra in the wavelength range of ~350-835 nm. For 532-nm excitation of I_2–BEN, I_2–TOL, or I_2–MES solutions, no absorption bands besides the tailing absorption of the I–arene complex were observed in the 630-nm to 835-nm region at times ranging from -8 to ~50 ps after excitation.

In regard to the presence of $I_2^-\cdot$, this radical anion has been reported to exhibit an absorption maximum at ~370 nm.[16] For those measurements,[16] $I_2^-\cdot$ was generated by means of microsecond-pulsed excitation of aqueous I^-, presumably via

$$I^- \xrightarrow{h\nu} I\cdot + e^-$$

$$I\cdot + I^- \rightarrow I_2^-\cdot$$
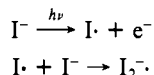
However, electron attachment to I_2 is dissociative, proceeding via the $^2\Pi$ g repulsive state to give I^- and $I\cdot$.[17] This dissociative electron attachment is akin to the process that would give rise to $I_2^-\cdot$ via CT excitation of an I_2–arene complex. Therefore, $I_2^-\cdot$ generated in this manner probably has a lifetime of < 10 ps and would not be detected in our experiment. Indeed, interrogation of I_2–TOL and I_2–MES in the 360-nm to 395-nm region, after sample excitation at 532-nm, provides no evidence for the existence of a transient absorption at ~370 nm that could be assigned to $I_2^-\cdot$.

Although we cannot detect the presence of $I_2^-\cdot$, we assign the early time-dependent absorbance changes in the transient absorption spectra to the rapid formation and decay of the respective arene cation radical. $BEN^+\cdot$, $TOL^+\cdot$, and $MES^+\cdot$ are expected to exhibit absorption bands in the region of 400-500 nm. From the photodissociation spectra of several methyl-substituted benzene ions, the visible absorption bands of $TOL^+\cdot$, $MES^+\cdot$, and $HMB^+\cdot$ (hexamethylbenzene cation radical) in the gas phase exhibit maxima at 416, 456, and 463, respectively.[18] Of course, shifts of γ_{max} are expected from the gas phase to solution. A basis for

comparison of gas-phase and solution absorption spectra is provided by the $HMB^+\cdot$ absorption spectrum with $\lambda_{max} \cong 495$ nm in acetonitrile[19] vs. $\lambda_{max} = 463$ nm in the gas phase nm in the gas phase. Also, $TOL^+\cdot$ exhibits an absorption maximum at 430 nm in a frozen argon matrix.[20] From these observations, we expect absorption maxima in solution at wavelengths that are ~20-30 nm longer than those given in ref 18 that are based upon photodissociation spectra.

In the time-resolved spectra presented in Figures 1-5, the absorption spectrum of $AR^+\cdot$ also is superimposed upon the two time-dependent absorption spectra described previously, namely the bleach of ground-state I_2 absorption and the positive absorbance change corresponding to the formation of the I–AR complexes. These superpositions make a quantitative and qualitative evaluation of the reaction mechanism outlined in Scheme I difficult. The I_2–MES samples provides the greatest separation among absorptions of $AR^+\cdot$, ground-state I_2, and I–MES complex for the series of solvents studied here. For excitation at either 355 or 532 nm, there is evidence for the presence of $AR^+\cdot$ and, therefore, for $[AR^+\cdot,I_2^-\cdot]$ as an extremely short-lived species.

In summary, our results indicate that photodissociation of I_2 in arene solution is affected to a certain extent by the fact that I_2 is weakly bound to an arene molecule. There is also evidence for the existence of the radical-ion pair $[AR^+\cdot,I_2^-\cdot]$ with a lifetime of < 10 ps but no experimental evidence of a cage effect involving recombination of two I atoms. We also observe that identical time-dependent absorbance changes occur at times less than ~4 ns for excitation of I_2 solutions in BEN, TOL, and MES regardless of excitation wavelength. Specifically excitation either at 355 nm, a wavelength within the CT absorption band of the I_2–AR complex, or at 532 nm, a wavelength associated with absorption of light by the I_2 molecule, which is bound, to a significant extent, to an arene molecule generates the same species.

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Comparison of Gas-Phase and Electrochemical Hydrogenation of Ethylene at Platinum Surfaces

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Abstract: Rates of hydrogenation of ethylene to ethane under gas–solid (G–S) and liquid–solid (L–S) (i.e., electrochemical) conditions at well-defined Pt(111) and smooth polycrystalline Pt surfaces are compared. The activation energies are 5.9 kcal/mol for the L–S reaction and 10.8 kcal/mol for the G–S reaction. Comparison of the rate laws under appropriate conditions shows that the hydrogenation proceeds by different reaction mechanisms at the two different interfaces. We have used surface science techniques (low-energy electron diffraction, Auger electron spectroscopy, high-resolution electron energy loss spectroscopy, temperature-programmed desorption) and electrochemistry (a combination of solution and ultrahigh vacuum procedures) to characterize the adsorbed species formed under G–S and L–S reaction conditions and gain insight into the reaction mechanisms. We propose that in hydrogenation at the L–S interface, ethylene is reduced on the Pt surface by adsorbed H atoms, while during hydrogenation at the G–S interface, H atoms must be transferred from the Pt surface through a layer of irreversibly adsorbed ethylene to ethylene that is adsorbed on top of this layer.

One of the fundamental questions of surface chemistry is how chemical changes that occur at gas–solid (G–S) interfaces compare

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with those at the liquid–solid (L–S) interface. These two heterogeneous processes are intrinsically similar—both involve mass transfer to and from the surface, adsorption, desorption, and chemical reactions at the surface (Figure 1). However, the molecular structures and chemical reactions in the interfacial regions are possibly quite different due to the effects of higher molecular flux, solvent, and electrode potential at the L–S interface. Consequently, atomic surface structure, adsorption, and