

17 and Table I, respectively), to the hydration of the zwitterion clustering, compared with 8 kcal/mol for two more neutral hydrogen bonds. Therefore, solvation by four water molecules would be sufficient to make the transition to the zwitterion exothermic by 12 kcal/mol.

The above estimate considers the two ionic functions in the zwitterion to hydrogen bond as separate ions. In fact, the presence of the opposite charge in the molecule will decrease the charge on each group, which weakens the hydrogen bonds at each site and creates a situation more analogous to neutral hydrogen bonds. Therefore, solvation by substantially more than four water molecules may be necessary to make the formation of zwitterions exothermic.

The present data also demonstrate that OH⁺...O hydrogen bonds can make substantial contribution to protein conformation and enzyme action. For example, carboxylic functions of aspartic acid and glutamic acid residues are found near the active sites in enzyme cavities. The present data show that if optimal geometric alignment is allowed, such ionized carboxylic functions may form bonds as strong as 30 kcal/mol with neutral OH or COOH groups in the enzyme or the substrate.

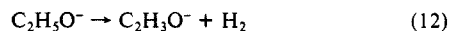
Experimental Section

The measurements were carried out with the NBS pulsed electron beam mass spectrometer, which has been described elsewhere.¹⁸ Negative ions were generated by adding an electron scavenger, such as C₂H₅NO₂, N₂O, CH₃ONO, or SF₆ (for carboxylic acid reaction systems) to the carrier gas, which was CH₄ or *c*-C₆H₁₂. In some cases, neat N₂O or SF₆ was used as the carrier gas. The primary anions, formed by electron capture or dissociative electron capture, reacted rapidly with the sample components to yield the RO[−] and RCOO[−] ions of interest.

For all equilibria, checks were made to ensure that the equilibrium constant was independent of total source pressure and of the partial pressure of the ligand. In particular, CH₃O[−]·CH₃OH was checked thoroughly because of a discrepancy of our value for Δ*H*[°], 28.8 kcal/mol, with a low value, 21.8 kcal/mol, quoted in ref 6. For this reaction, we obtained van't Hoff plots by using neat N₂O and by using 2% N₂O in *c*-C₆H₁₂ as carrier gases, and another van't Hoff plot was obtained for CD₃O[−]·CD₃OD by using trace N₂O in CH₄ as a carrier gas. Further, we did detailed studies with varying partial pressures of CH₃OH at three temperatures, varying the concentration of CH₃OH between 0.2 and 2.0 × 10¹⁴ molecules/cm³. The results of all of the studies were consistent

within ±1 kcal/mol for Δ*H*[°] and ±2 cal/(mol·K) for Δ*S*[°], which are our usual error limits.

To study the cluster C₂H₅O[−]·C₂H₅OH, we used C₂H₅OH in CH₄ and trace N₂O as the carrier gas. In this system, we observed the overall reaction



The reaction appeared to be catalyzed by the presence of C₂H₅OH, i.e., the apparent first-order rate constant increased with increasing concentration of C₂H₅OH. The apparent second-order rate constant was ~10^{−10} cm³ s^{−1} at 600 K and showed a small positive temperature coefficient. The observed high rates ruled out reactions with an impurity, e.g., CH₃CHO, as the source of the product C₂H₃O[−] ion. Analogous dehydrogenation reactions were observed with *n*-C₃H₇O[−] and *i*-C₃H₇O[−]. Because of reaction 12 and its dependence on the concentration of C₂H₅OH, the clustering studies in this system were carried at a low concentration, 0.0001, of C₂H₅OH.

For measurements involving other symmetric dimers (RO[−]·ROH and RCOO[−]·RCOOH) the sample ROH and RCOOH compounds were usually 0.01 or less of the total gas mixture in the ion source. For RCOO[−]·H₂O, RCOO[−]·ROH, C₆H₅O[−]·H₂O, and C₆H₅O[−]·ROH, however, the formation of RCOO[−]·RCOOH and C₆H₅O[−]·C₆H₅OH dimers competed with the equilibria under study, and in some cases the formation of these dimers depleted the monomer anions irreversibly. When this occurred trace amounts, less than 0.0001 of RCOOH and C₆H₅OH, and large amounts, up to 0.50 of the reaction mixture, of H₂O and ROH were used to slow the depleting reactions and maximize the formation of the complexes of interest. In some systems, such as CH₃COO[−]·H₂O, van't Hoff plots were obtained at various concentrations of CH₃COOH to verify that the competing dimerization did not effect the results for the thermochemistry of CH₃COO[−]·H₂O.

The total gas pressure in the ion source was in the range of 0.5–2.5 torr. Checks were made to demonstrate that the measured equilibrium constants were independent of total source pressure and mixture composition.

The chemicals were obtained from commercial sources, with nominal purities of 98% or greater, and used as supplied.

Acknowledgment. We thank Dr. W. Stevens for unpublished results of ab initio calculations. This work was supported in part by the Office of Basic Energy Sciences, U.S. Department of Energy.

Registry No. C₂H₅O[−], 16331-64-9; *i*-C₄H₉O[−], 16331-65-0; C₆H₅O[−], 3229-70-7; HCOO[−], 71-47-6; C₂H₃O[−], 35731-40-9; CH₃COO[−], 71-50-1; (CH₃)₂CHCOO[−], 5711-69-3; CF₃COO[−], 14477-72-6; C₂H₅OH, 64-17-5; H₂O, 7732-18-5; CH₃OH, 67-56-1; CH₃CO₂H, 64-19-7; HCO₂H, 64-18-6; C₆H₅OH, 108-95-2; H₃CO(CH₂)₂O(CH₂)₂OCH₃, 111-96-6; (C-H₃)₂CHCO₂H, 79-31-2.

Selectivity in the Laser-Induced Photochemistry of I₂ + C₂H₂ in the Gas Phase

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Abstract: The reaction between I₂ and acetylene has been carefully studied to establish its potential use for the separation of radioactive isotopes of iodine. The two possible photoproducts, *cis*- and *trans*-1,2-diiodoethylene, were prepared and then characterized by GC, GC-MS, and FTIR in both condensed and gas phases. For the first time the IR spectra of both *cis* and *trans* isomers in the gas phase are reported. Below the dissociation energy, when either the ortho or para modifications of I₂ were excited, only the *trans* isomer was found as a product. Studies conducted with isotopic mixtures of ¹²⁷I₂, ¹²⁹I₂ and ¹²⁷I, ¹²⁹I revealed that the reaction proceeds by the addition of iodine atoms to acetylene. The production of atoms leads to isotopic scrambling. Consequently, this reaction cannot be used to separate the isotopes of iodine, as previously postulated.

The reaction between halogens, especially iodine, and hydrocarbons is extensively documented in the chemical literature.¹

Surprisingly, there is still confusion about the gas-phase photochemical addition of iodine to unsaturated hydrocarbons, for

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example, acetylene. This reaction is particularly interesting because of the possibility of *cis* vs. *trans* products, stepwise attack by atoms vs. one-step molecular addition, potential effects of vibrational and rotational energies, the effects of excited I atoms, the presence of ortho vs. para modifications, and potential isotopic selectivity. It is also one of the more spectacular reactions due to the visible fluorescence of I_2 and the production of condensable material directly in the light beam.

The separation of isotopes by laser light has been an active area for research since the first demonstration.² Radioactive iodine is a byproduct of nuclear fission³ and is also used clinically as an isotopic tracer.⁴ The ability to separate iodine isotopes is therefore of practical importance. Early experiments have shown that the fraction of ortho vs. para iodine can be altered by photochemical reaction with hexene.⁵ When ortho- I_2 alone is irradiated in the gas phase in the absence of hydrocarbon, the normal ortho/para ratio can also be altered if the excitation intensity is reasonably high.⁶ The fact that both ortho and para concentrations decreased during irradiation makes interpretation of the mechanism difficult. Also, since the two species reequilibrate back to the normal ratio of 5/7 in the time scale of an hour and since the maximum enhancement for the ortho species is only a factor of 2, this separation procedure has little real utility. When 2-hexene is added as a scavenger, enrichment of para- I_2 is found if ortho- I_2 is irradiated.⁷ It is surprising that the enhancement factor is only 4 under optimized conditions. It is also surprising that the reaction rate is independent of I_2 pressure for a fixed laser power but dependent on laser power for a fixed I_2 pressure. If excited I_2 is involved in the reaction (atomic or molecular photochemistry), then the reaction rate should be related to the production of excited I_2 , which is simply the product of I_2 pressure and laser power under these conditions. The results reported for reaction with C_2H_2 are even more confusing. Both *cis*- and *trans*-diiodoethylene were reported as products,⁸ while it has been well-established that these reactions follow a *trans* addition, *cis* elimination pathway.⁹ The *trans* isomer was reported to be stable thermally and photochemically to conversion to the *cis* form in the presence of iodine if irradiated at 514 nm but not if irradiated at 488 nm.⁸ The implication is that excited iodine atoms produce the *cis* product while ground-state iodine atoms produce the *trans* product. While addition to acetylene was observed at these wavelengths and at 604 nm,¹⁰ no reaction between I_2 and hexene was observed at 488 nm or 590 nm.⁷ It is also not clear why the mixed isotopic product ($C_2H_2I_2$) was formed (Figure 2A of ref 10) when no mixed isotopic reactant (I_2) was present and broadband radiation was used. This is inconsistent with the fact that the reaction is isotopically selective (Figure 2B of ref 10).

To clear up the above questions, we have reinvestigated the photochemical reaction between I_2 and C_2H_2 . Positive product identification was made based on GC, GC-MS, and vapor-phase IR spectra. Excitation was controlled by using a single-frequency dye laser. Product collection was studied in the gas phase. Selected mixed-isotope and ortho-para studies were performed. A cohesive picture of the reaction can thus be obtained.

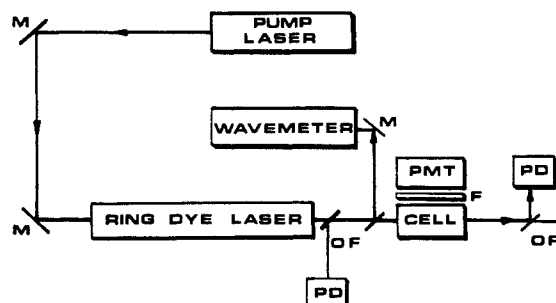


Figure 1. Schematic diagram of instrumental setup: M1, M2, M3, mirrors; OF, optical flats; PD, photodiode; F, filter.

Experimental Section

***trans*- and *cis*-1,2-Diiodoethylene.** The *trans*-diiodoethylene was prepared according to ref. 1a by passing acetylene into a solution of iodine (J. T. Baker 2211) in absolute ethanol for 10 days. At that time some needlelike crystals could be seen on the reaction vessel. The addition of a 8 g/L solution of NaOH produced the precipitation of a yellowish, fluffy mass of crystals. These crystals were then filtered and washed with the NaOH solution and then with double-distilled water.

The pure *trans* isomer was obtained by subliming the previously obtained crystals under atmospheric pressure. The white needlelike crystals have a melting point of 73 °C and very sharp odor. *cis*-1,2-Diiodoethylene was prepared according to Noyes^{1a} by heating the *trans* isomers and a trace amount of I_2 for 72 h at 165 °C. Part of the *trans* isomer still present in the mixture was removed by condensing it on the cold finger of the sublimation apparatus. Pure *cis*, however, was not obtained.

Isotopic Mixture of Iodine. An ampule containing 200 mg of iodine crystals was purchased from Oak Ridge National Laboratory. A solid probe of the mixture was analyzed by MS. The mixture contains 73.5% of $^{129}I_2$, 24.5% of $^{127}I^{129}I$ and 2.0% of $^{127}I_2$.

Gas Chromatograph. A Tracor 550 gas chromatograph equipped with a 3% Dexsil 300 80/100 Chromosorb WAW packed column and electron capture detector (ECD) was used in this work. Argon with 10% methane was used as the carrier gas. The column temperature was kept at 45 °C. Higher temperatures and/or temperature programs did not allow the resolution of the two isomers. The ECD detector and inlet temperatures were 340 and 110 °C, respectively.

GC-MS System. A Finnigan 4000 GC-MS upgraded with a 4500 ion source was used. A DB-1, 30-m fused silica capillary column from J & W scientific with 0.26-mm i.d. and a film thickness of 0.25 μm was used for the separation of the isomers. For the studies with isotopic mixtures, multiple ion detection was chosen over the more frequently used mass scanning technique in order to achieve greater sensitivity. The ions of mass 127, 129, 254, 256, 258, 280, 282, and 284 were monitored.

FT-IR Spectrometer. The IBM IR 98 computer-controlled FT-IR spectrometer was configured for the mid-IR (400–4000 cm^{-1}). The maximum resolution used was 0.5 cm^{-1} . The same reaction cell equipped with NaCl windows was used in the FTIR spectrometer.

Instrumental Setup. Figure 1 shows the instrumental setup used for inducing the photochemical reaction and for taking absorbance and fluorescence measurements. The pump laser is an Ar⁺ laser (Model 554 A from Laser Ionics) equipped with broadband mirrors. The ring dye laser is a Spectra Physics Model 380 A (Rhodamine 6G) with a resolution better than 0.002 cm^{-1} .

A WA-20 Wavemeter from Burleigh was used to measure the frequency output of the ring dye laser. The system has an accuracy of 0.01 cm^{-1} . The reaction cell is a gas beta cell, 10-cm pathlength, Pyrex glass, purchased from Buck Scientific Inc. The two inlets were modified to be directly connected to a greaseless vacuum system which used "O" ring joints and Teflon stopcocks. Pressure levels of less than 10^{-5} T are reached with this vacuum system equipped with a diffusion pump.

For the absorbance (ABS) measurements the intensity of the beam was monitored before and after the cell. The monitor output from the laser system was used as a reference to compensate for changes in laser intensity. A portion of the beam transmitted through the cell was directed to a photodiode (Hamamatsu Corporation, Middlesex, NJ Model S1790). Both signals were fed to a PDP-11/10 minicomputer. The software was designed to acquire dark, blank (outside the absorption band), and transmitted signals. The average and standard deviation of 100 consecutive measurements was displayed and stored.

For fluorescence (FL) measurements, a photomultiplier tube (PMT, Hamamatsu Corp. Middlesex, NJ, Model R928) supplied with ~ 370 V (by Hamner HV Power Supply) was placed parallel to the cell axis. A cut-off filter (Corning Glass, Corning, NY, Model 2-62) was placed in

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Table I. Infrared Spectral Data and Assignments for *trans*-IHC=CHI and *cis*-IHC=CHI

| species | ω_0 | ω'_0 | assignment | |
|---------|------------|-------------|--------------------------|-------|
| trans | 600 | 586, 589 | σ_{11} | b_u |
| | 599 | | | |
| | 596 | | | |
| cis | 642 | 645 | σ_{12} | b_2 |
| cis | 682 | 672 | σ_{10} | b_1 |
| | 680 | | | |
| | 677 | | | |
| trans | 729 | 733 | | |
| trans | 915 | 908 | | |
| trans | 1134 | 1126, 1130 | σ_{10} | b_u |
| | 1130 | | | |
| | 1231 | | | |
| cis | 1237 | 1219 | σ_9 | b_1 |
| cis | 1312 | 1307 | $\sigma_5 + \sigma_9$ | b_1 |
| cis | 1510 | 1512 | $\sigma_3 + \sigma_{11}$ | b_1 |
| | 1520 | | | |
| | 1545 | | | |
| trans | 1557 | 1547 | σ_2 | a_1 |
| | 1615 | | | |
| | 1620 | | | |
| cis | 3053 | 3023 | σ_8 | b_1 |
| | 3058 | | | |
| | 3083 | | | |
| trans | 3087 | 3062 | σ_9 | a_g |

^a ω_0 observed frequency, this work. ^b ω'_0 from ref 12.

front of the aperture of the PMT housing to minimize the contribution of scattered light to the FL signal.

Results and Discussion

Characterization of *cis*- and *trans*-1,2-Diiodoethylene. The chromatograms obtained with GC-ECD and GC-MS for the *trans* isomer and for a mixture of both isomers are used for product identification, since the pure *cis* isomer was not available. Base line separation was obtained. The mass spectra for both isomers show the same ions, confirming the identity of the prepared compounds. The elution order obtained with the capillary column, which has very low polarity, is *cis*, *trans*, as expected from the melting points of the isomers (*trans*, 73 °C; *cis*, -13 ± 1 °C).¹¹ However, the elution order is reversed in the packed column with higher polarity. This is due to the higher polarity of the *cis* isomer, which causes longer retention as compared to the *trans* isomer. So, retention times must be interpreted with care for product identification.

FTIR was chosen as an independent technique for confirmation of the identity of the two possible photoproducts. The gas-phase spectra showing the strongest bands for both isomers are shown in Figure 2a-e. These have not been recorded previously. Previous IR spectra¹² were published for solutions of the isomers in CCl_4 and CS_2 . Thus, the band contours are not very useful for band assignments. Table I shows the frequencies recorded in this work and those previously published. These results show that the previously reported IR spectrum for the photochemical products⁸ is in error. The sensitivities of GC-ECD and GC-MS detection techniques are greater than that for FTIR by approximately 2 orders of magnitude under these experimental conditions.

Photoreaction of *ortho* and *para* I_2 with C_2H_2 . The I_2 molecule is composed of two identical nuclei with nuclear spin $I = 5/2$. As result, the molecule exists in two modifications: *ortho* I_2 with odd total nuclear spin and *para* I_2 with even total nuclear spin. Selection rules dictate that, in the ground electronic state, the former exists only in *odd* rotational levels and the latter exists only in *even* rotational levels. The influence of the type of modification excited on the reaction products was investigated. The possibilities

Table II. Isotopic Compositions Before and After Laser-Induced Reaction

| conditions | % of $C_2H_2I_2$ | | | |
|--|-------------------|-----------|-------------------|------|
| | $M = 280$ | $M = 282$ | $M = 284$ | K |
| A "dark" products (60 min) $^{129}I_2 + C_2H_2$ (21T) | 3.8 | 17.7 | 78.5 | 0.94 |
| A' photoproducts (70 min) 17014.09 cm^{-1} ($^{129}I_2$) | 1.4 | 24.8 | 73.8 ^a | |
| B "dark" products (70 min) $^{129}I_2 + ^{127}I_2 + C_2H_2$ (20 T) | 38.9 | 44.7 | 16.4 | 0.93 |
| B' photoproducts (68 min) 17228.03 cm^{-1} ($^{129}I_2$) | 38.6 | 46.1 | 15.3 ^a | |
| C "dark" products (115 min) $^{129}I_2 + ^{127}I_2 + C_2H_2$ (25T) | 15.4 | 32.7 | 57.9 | 0.87 |
| C' photoproducts (150 min) 17166.77 ($^{127}I_2$) | 13.4 ^a | 32.0 | 54.6 | |
| D "dark" products (60 min) $^{129}I_2 + ^{127}I_2 + C_2H_2$ (200 T) | 24.3 | 47.8 | 27.9 | 0.95 |
| D' photoproducts (50 min) 17226.39 cm^{-1} ($^{127}I_2$) | 23.1 ^a | 47.7 | 29.2 | |

^a Species containing the excited iodine isotope.

of different rates of reaction and of obtaining different isomers (*cis* or *trans*) depending on the type of modification excited had not been previously considered.

The selection of excitation energies was based on previous spectral assignments.^{13,14} Even though the B-X system for I_2 has been extensively studied, the agreement among researchers on the assignment of rotational quantum numbers to precisely measured frequencies is quite poor. The lines chosen for this investigation are those for which at least two references^{13,14} agree in the transition assignment and in their frequencies within 0.03 cm^{-1} . These lines correspond to the R branch of the 14-1 transition and lie at 17012.09 cm^{-1} for $J = 93$ (*ortho*) and 17014.06 cm^{-1} for $J = 94$ (*para*). A third line at 17012.25 cm^{-1} ($J = 89$) corresponding to P branch of the same band was used as well. Even though these lines do not lie in the spectral region of maximum power output for our dye laser, the average power (~ 45 mW) was sufficient for the photochemical reactions. The ABS of the mentioned transitions was measured first at high resolution to verify their spectral locations and to ensure their resolution from adjacent lines. In previous studies,^{6,7} the output of an Ar laser was used to excite the iodine molecules. The halfwidth of the lines used (4880 and 5145 Å) is approximately 2 Å. Therefore, several transitions corresponding to both I_2 modifications were simultaneously excited.

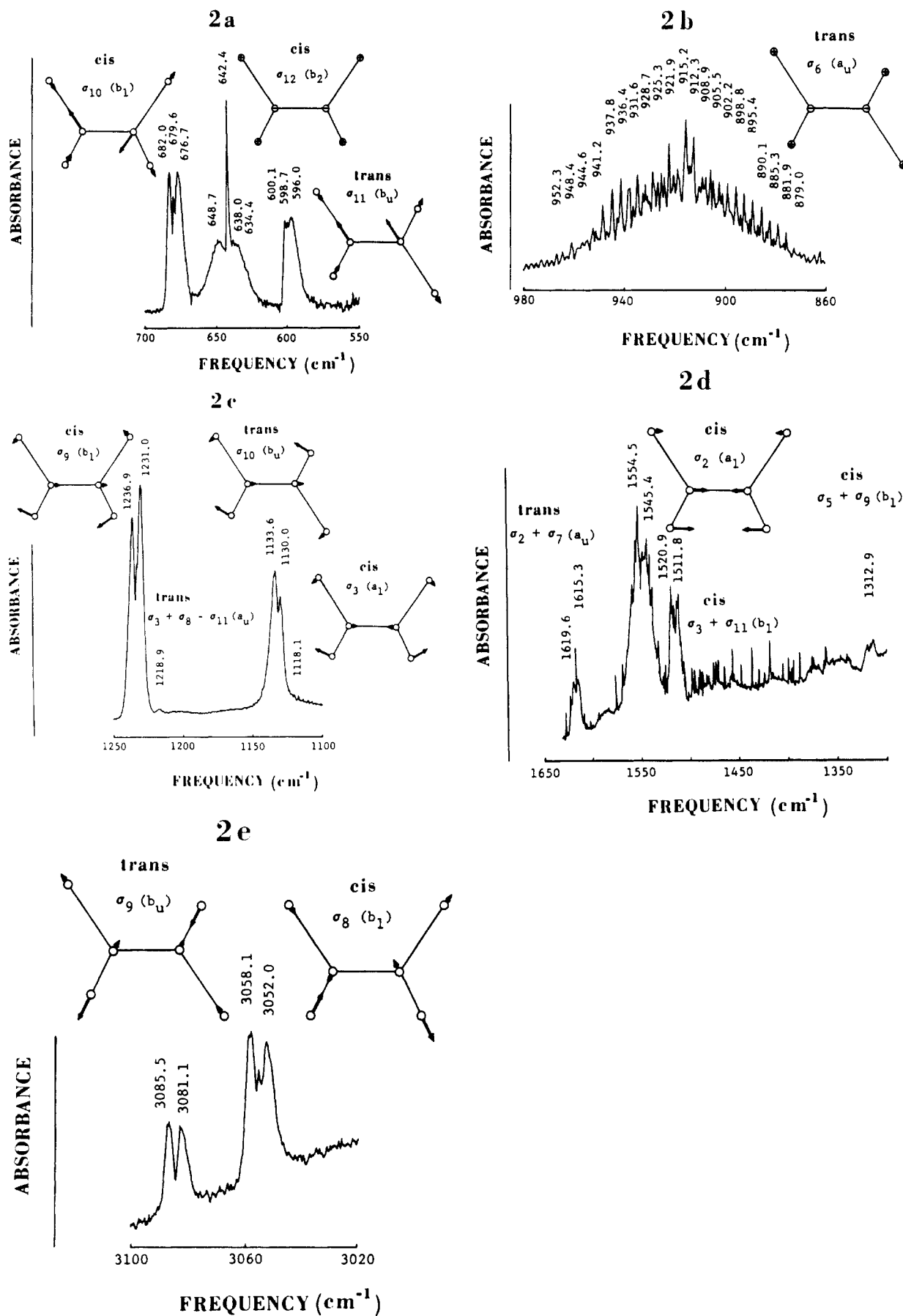
The sampling of the reaction products could be done by condensation of reaction products in a cold trap with subsequent dilution in pentane. However, this technique was not pursued for two reasons. The sample analyzed must be representative of the composition inside the cell. If the products are not totally and efficiently condensed, the results are not useful. Also, in the condensed phase, the possibility of isomerization of the products (*cis* and *trans*) could be enhanced, and the results would be misleading. Because of these considerations, sampling was done in the gas phase. Typically, volumes of 0.5–1.0 mL are withdrawn by a gas syringe. Time dependent studies were conducted to ensure that at the time of sampling the vapor pressure had not reached its maximum value due to product accumulation (condensation). Otherwise, the relative amounts of the possible photoproducts could not be determined properly. Figure 3 shows the results obtained when exciting the reaction mixture at 17012.09 cm^{-1} (~ 40 mW). The maximum level of gas-phase photoproduct is reached in approximately 40 min. Thus, reliable sampling was only possible

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Figure 2. FT-IR gas-phase spectra of *cis*- and *trans*-1,2-diiodoethylene in various spectral regions.

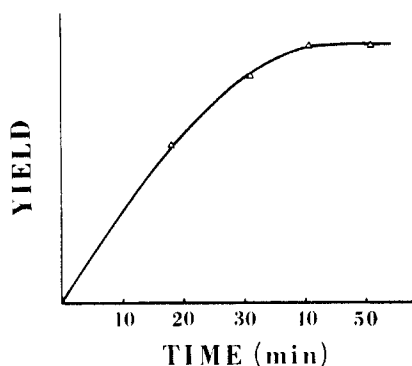


Figure 3. Yield of $C_2H_2I_2$ as a function of irradiation time. About 40 mW of 17012.09 cm^{-1} light was used.

within the first 20 min of reaction, where the curve is linear.

For a C_2H_2 pressure of 25 T, at the three dye laser frequencies (40 mW) and when using the Ar beam (200 mW), only the trans isomer was observed as a product. When the C_2H_2 pressure was varied from 5 T to 100 T and excited with the Ar laser beam at 200 mW, no cis isomer was observed. These results were confirmed by FTIR. The only reactions that yielded a trace amount of cis (3% or less of the trans isomer) were those excited with the Ar laser at 2.0 and 3.5 W for periods longer than 30 min. Previous publications had postulated the formation of the cis isomer by atomic addition under radiation at 488 nm.⁸ Our results do not support such a hypothesis. In fact, no cis isomer was observed even when the photoreaction was induced at 325 nm with a HeCd laser with ~ 3 mW of power for 60 min. This suggests that the cis isomer is formed by a thermal, rather than photochemical process. Such a mechanism is consistent with the thermal conversion of trans to cis in the presence of iodine.¹¹

Reaction of C_2H_2 with Isotopic Mixtures of Iodine. The dark and photochemical products, respectively, were analyzed by GC-MS to determine the isotopic composition before and after the selective excitation of a single isotope. Table II lists the results obtained together with the selectivity coefficients K , calculated as the ratio of the relative amounts of the isotopic species of interest after and before photoexcitation. The dark reaction is nonselective and thus the relative amounts give the initial isotopic composition

of the reactants. This is a necessary measurement because the relative amounts of the three isotopic species of I_2 are difficult to determine directly at the start of the reaction, e.g., by selectively mixing the isotopic species of I_2 . The quantities indicated as "photoproducts" represent the total amounts detected after the reaction minus the "dark" product extrapolated at the time of termination of the laser excitation. Such corrections are all 3% or less of the net photoproduct. In all cases the selectivity coefficient is near unity, indicating that scrambling occurs.

If the reaction proceeded by the addition of excited I_2 molecules to the C_2H_2 molecules, the K values would have been much greater than unity. So, we can conclude that the reaction occurs by addition of atoms to the C_2H_2 molecule. Furthermore, the severe scrambling observed indicates that such atoms do not come from the excited molecule only. Isotopic exchange in the gas phase or at the cell walls is known to be important.^{7b}

Conclusions

The photochemistry of $I_2 + C_2H_2$ was reinvestigated by using single-frequency excitation, gas-phase product analysis, gas-phase FTIR identification of isomers, and GC-ECD and GC-MS measurements. Only trans $C_2H_2I_2$ is formed in the photochemical reaction regardless of excitation wavelength. *cis*- $C_2H_2I_2$ and $-C_2H_2I_4$ are formed as secondary reaction products, with the former going through a thermal, I atom assisted isomerization of the trans isomer. Gas-phase IR spectral band assignments reported here for *trans*- and *cis*- $C_2H_2I_2$ indicate that previous spectra^{8a} are in error. Isotopic studies show complete scrambling in the products, confirming reaction by stepwise I atom addition. This implies that isotope separation of I_2 is not possible with this reaction scheme, in variance with earlier reports.¹⁰ It seems that adsorption of I atoms on the walls of the reaction vessel is primarily responsible for a small degree of isotopic or ortho/para selectivity observed as the depletion of the species being excited. However, the low degrees of enhancement and the lack of a stable isotopic product precludes any practical utility.

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Registry No. C_2H_2 , 74-86-2.

Some Tentative Models of Molecular Motion Applied to Water in Small Reversed Micelles

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Abstract: The molecular dynamics of water in small, swollen, reversed micelles of sodium bis(2-ethyl-1-hexyl)sulfosuccinate (AOT) in cyclohexane has been investigated using proton NMR relaxation methods. When the water content drops from 15 to 3 molecules per AOT molecule, the 1H NMR relaxation time T_1 is considerably reduced. This is due in part to slower motions of water molecules and also to the increased influence of external relaxation processes, such as the dipolar interactions with the surfactant protons. By progressive substitution of the micellized water by heavy water, the dipolar water-water effects have been distinguished from other relaxation processes. Using standard models of motion, this substitution has shown the water movements to be slower than in pure water by at most a factor of 5. This somewhat unusual result is in agreement with data from concentrated ionic solutions. The external relaxation effects displayed a frequency dependence which is typically induced by slow motions. Some dynamical models have been discussed to explain them, but the main effects seem to be induced by the dipole-dipole interaction with the protons of the AOT polar heads. The complex modulation of this interaction could not be described precisely, and a simplified model was used to deduce qualitative dynamical information from the experimental data. The water-polar head movements were then found to be in the range of 5×10^{-10} s.

For the last few years investigations on microemulsions and micellar systems have been greatly stimulated by possible applications in industry and in other scientific fields (biology,

chemistry, etc.), as well as by the very specific phenomena these systems display. A reversed micellar system is a solution of spheroidal aggregates of amphiphile molecules in an aliphatic