Product Yields from Multiphoton Processes in Cyclohexane and Solutions of Aromatic Compounds[†]

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Products from the 248 nm photolysis of neat cyclohexane are measured as a function of light intensity and total exposure. The yields of these products increase in proportion to the square of the incident intensity, indicating a biphotonic process, and the quantum yields are independent of the total incident light. The quantum yields (per two photons absorbed) are 0.6 ± 0.1 , 0.6 ± 0.1 , and 0.04 ± 0.01 , for H₂, cyclohexene, and bicyclohexyl, respectively. These quantum yields indicate that molecular decomposition (to H₂ and cyclohexene) of excited cyclohexane resulting from the geminate recombination of electron-solvent radical cation pairs created in the biphotonic ionization process accounts for more than 80% of the ions. For a given incident light intensity, the addition of an aromatic solute (anthracene, biphenyl, or acenaphthene) causes the amount of these products observed to increase, despite the fact that the light absorption by the solvent is markedly less. This indicates the occurrence of processes by which energy absorbed by an aromatic molecule results in decomposition of the cyclohexane. Evidence that this process is proton transfer from excited aromatic radical cations is discussed.

Introduction

Alkane liquids and solutions of aromatic compounds are readily ionized using UV excimer lasers.¹ Work recently reported from our laboratory quantitatively examined the conductivity signals induced, and the results were discussed in the context of a mechanism in which formation of protonated solvent molecules plays an important role.² To gain more insight into the importance of this process, we have extended previous product yield determinations that have been made in such systems,^{1,3,4} by examining intensity, exposure, and solute concentration effects and by determining quantum yields.

Experimental Section

Sample Preparation and Photolysis. The irradiation cell was a 4×4 mm quartz spectrophotometer cell (from Starna Cells, Inc.) modified by joining it to a threaded cap that allows the cell to be fitted with a septum. A special cell holder was made to allow positioning of this cell into a standard 10×10 mm spectrophotometer cell holder.

The cyclohexane used was Burdick & Jackson high-purity grade, passed through 1 m columns of activated silica gel. The aromatic compounds were from Aldrich, 99.9% grade, used as received. Unless otherwise noted, air was purged from solutions by bubbling with argon. This was done by inserting two needles through the septum into the irradiation cell: one was connected to the source of argon and one was connected to a 3 mL syringe that contained the sample. Typical bubbling times were about 10 min. After degassing, the sample is allowed to flow through the needle into the cell. The volume of the sample was determined from the density of cyclohexane by weighing the cell before and after filling. This volume was needed to calculate concentrations of products from the gas chromatography results. The empty cell volume (ca. 1 mL) was needed to determine the total hydrogen produced from the gas chromatography results on an aliquot of the gas volume above the sample.

The photolysis was done with pulses of 248 nm light from an excimer laser (Lumonics HyperEx-420, 15 ns pulse at 2 s^{-1}). A lens system was use giving a light beam with dimensions of $\sim 3 \times 10$ mm at the entrance slit on the cell. An area of 0.15 $\times 4.0$ mm was taken from the central part of the beam using an aperture at the front of the sample cell. The light passing through the cell was collected by a third lens, and its power was measured by a laser power meter (ED-500 Joule meter and EM-1 Readout device, both made by Gentec). The relative intensity of the laser beam before the aperture in front of the sample cell was monitored by splitting part of the light to a photodiode, as we have described previously.²

In photolysis of neat cyclohexane, the samples were pulsed at 2 s⁻¹ continuously until the desired number of pulses was accumulated. In the photolysis of solutions containing aromatic solutes the photolysis was done in groups of pulses, the sample being shaken between groups in order to replenish the solute in the irradiated zone. (The aromatic solute disappears in what seems likely to be a one-photon process, based on separate experiments on biphenyl solutions using a continuous, lowintensity light source). In typical runs using 10.5 mJ pulses through the 0.06 cm² aperture, a few tenths of a percent of the aromatic solutes disappeared per pulse. The disappearance rate was observed to be qualitatively greater the greater the oxygen contamination of the sample.

Gas Chromatography. Measurement of H_2 : Hydrogen gas was measured using a SRI 8610 gas chromatograph equipped with a four-filament thermal conductivity detector, using argon carrier gas. A molecular sieve 5A column was used at ambient temperature. Calibration was done by injecting 100 μ L of a mixture of H_2 and air (1:1). The detection sensitivity (area per micromole) is $(7.0 \pm 0.2) \times 10^5$ for hydrogen, $(7.50 \pm 0.2) \times$ 10^4 for oxygen, and $(5.8 \pm 0.2) \times 10^4$ for nitrogen. Analysis of photolyzed samples was done by withdrawing 0.5 mL from the vapor phase in the photolysis cell using a 1 mL gas-tight

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syringe (Pressure-Lok, Precision Sampling Corp.), which had been flushed with argon before taking the sample. Equilibrium between the liquid and vapor phase was attained by shaking before withdrawal of the aliquot. Successive aliquots gave the expected relative amounts of hydrogen. The syringe was then turned to the "locked" position, the needle was pulled out of the photolysis cell, and the sample was injected into the gas chromatograph. Hydrogen was well separated from air, making the analysis quite straightforward; the retention times were 0.80 min for H₂, 1.70 min for O₂, and 3.90 min for N₂.

Measurement of hydrocarbon products: Products dissolved in the cyclohexane liquid were measured using a Perkin-Elmer PE8500 gas chromatograph equipped with a split-splitless injector, a capillary column, and a flame-ionization detector. The column was a 30 m long by 0.25 mm i.d., DB5ms phase column (J&W Scientific), and helium was used as a carrier gas. Split injection was used for the analysis; 1 µL was injected and the injection block temperature was 320 °C. The peak for cyclohexene (2.16 min) is a shoulder on the tail of the cyclohexane peak ($\simeq 2 \text{ min}$). The split ratio was made as large as possible to obtain a good separation of cyclohexene from cyclohexane without making the relatively small (but well separated) signal from bicyclohexyl (10.9 min) too small to accurately measure. A temperature program was used which held the oven at 40 °C for the first 5 min and then increased the temperature to 300 °C in 10 min.

Calibration was done by injecting "known" solutions of cyclohexane containing cyclohexene and bicyclohexyl at various concentrations. For bicyclohexyl, the sensitivity was independent of the concentration, but for cyclohexene, a change with concentration was noted, apparently due to an artifact in the integration related to the fact that the cyclohexene peak is on the tail of the cyclohexane peak, making an accurate integration more difficult as the concentration becomes lower. Therefore, care was taken to calibrate for cyclohexene over the concentration range observed experimentally for the photolyzed samples. The sensitivities (in units of "area" per mole liter⁻¹) obtained for typical experimental concentrations are 1.4×10^7 and 3.9×10^7 for cyclohexene and bicyclohexyl, respectively.

Results and Discussion

Neat Cyclohexane. Figure 1 shows the yields per pulse of H_2 , cyclohexene, and bicyclohexyl vs the number of pulses. The results show that within about a $\pm 10\%$ spread the yields are independent of the total exposure. This shows that the accumulation of products (or consumption of impurities) has no effect on the product yields and strongly indicates that residual oxygen, or air leakage, is unimportant. Otherwise, a dependence of the bicyclohexyl yield on the number of pulses should have been observed due to the fact that at the intensities used oxygen would have scavenged cyclohexyl radicals before the radical-radical reaction occurred. Also, cyclohexanol and cyclohexanone, which are products observed in solutions of aromatics (see below), where oxygen contamination was a problem, were not observed.

Table 1 summarizes the average relative yields from Figure 1 for neat cyclohexane, normalized to unity for H_2 . (The yields for solutions are also given; they will be discussed below.)

Figure 2 shows a log-log plot of the intensity variation of the yields per pulse. The lines shown have slopes of 2. Within the experimental scatter, the product yields can be seen to follow this slope and are therefore indicated to result from biphotonic processes. This is in agreement with conductivity measurements, where the intensity dependence also indicates a biphotonic process.²



Figure 1. Product yields in micromoles per pulse vs number of pulses for the 248 nm photolysis (170 mJ cm^{-2}) of cyclohexane. The lines represent the average yields of each product.

TABLE 1: Relative Yields of Products from Cyclohexane^a

sample	H ₂	cyclohexene	bicyclohexyl
neat	1.00	0.91	0.074
$1 \times 10^{-4} \mathrm{M}$ anthracene ^b	1.45	1.20	0.19
$1 \times 10^{-4} \mathrm{M}$ biphenyl ^c	2.06	1.60	0.13
1×10^{-4} M acenaphthene ^c	2.85	1.78	0.13

^a For 170 mJ cm⁻² at 248 nm. ^b Most of the runs with aromatic solutes showed cyclohexanol and cyclohexanone as products, in amounts similar to bicyclohexyl. The results given for anthracene are from a run where no cyclohexanol or cyclohexanone was observed. The average yields of H₂, cyclohexene, and bicyclohexyl are 1.46, 1.04, and 0.15, respectively, for samples of 1×10^{-4} M anthracene in cyclohexano where cyclohexanol and cyclohexanone were observed, and the amount of cyclohexanol plus cyclohexanone is approximately equal to the difference between H₂ and the sum of cyclohexano and cyclohexano and cyclohexano bicyclohexyl. ^c The amount of cyclohexano and cyclohexano and cyclohexano bicyclohexano experimental bicyclohexyl. The amount of cyclohexano and cyclohexano and cyclohexano bicyclohexano bicyclohexano and cyclohexano and cyclohexano bicyclohexyl. The amount of cyclohexano and cyclohexano bicyclohexano and cyclohexano and cyclohexano bicyclohexano and cyclohexano and cyclohexano bicyclohexano bicyclohexano bicyclohexano and bicyclohexano bi

Considering the relative yields from neat cyclohexane, if ionic and excited-state processes result in only H_2 and cyclohexene (both produced molecularly), H atoms, and cyclohexyl radicals, one can easily show that the number of molecules of H_2 observed should equal the sum of cyclohexene and bicyclohexyl. Within experimental error, this is observed.

Another conclusion that can be drawn from the product yields from neat cyclohexane is that the processes leading to products favor molecular production (i.e., not through the intermediates H^{\bullet} or $C_6H_{11}^{\bullet}$) of H_2 and cyclohexene by about a 6 to 1 ratio. This observation is important in relation to the occurrence of reaction 1.

$$C_6H_{12}^{\bullet+} + C_6H_{12} \rightarrow C_6H_{13}^{+} + C_6H_{11}^{\bullet}$$
 (1)

If neutralization of $C_6H_{13}^+$ (reaction 2) is assumed to result in H_2 and cyclohexyl (via reaction 3), occurrence of reaction 1 can result in the formation of cyclohexene only by disproportionation of cyclohexyl radicals.

$$C_6 H_{13}^{+} + e^- \rightarrow C_6 H_{12} + H^{\bullet}$$
 (2)

$$\mathbf{H}^{\bullet} + \mathbf{C}_{6}\mathbf{H}_{12} \rightarrow \mathbf{C}_{6}\mathbf{H}_{11}^{\bullet} + \mathbf{H}_{2} \tag{3}$$



Figure 2. Log-log plot of product yields in micromoles per pulse vs incident intensity for the 248 nm photolysis of cyclohexane. The number of pulses used ranged from 130 at the highest intensity to 5000 at the lowest intensity.

$$C_6 H_{12}^{*+} + e^- \rightarrow C_6 H_{12}^{*+}$$
 (4)

(The possibility should be mentioned, however, that H_2 and cyclohexene could be formed if the H[•] from neutralization of $C_6H_{13}^+$ were to abstract an H[•] from the accompanying $C_6H_{11}^{\bullet}$ from reaction 1 before abstraction of H[•] from the solvent occurred). The self-reaction of two cyclohexyl radicals produces approximately equal amounts cyclohexene and bicyclohexyl $(k_{\text{recombination}}/k_{\text{disproportionation}} = 1.1^5)$. The large preponderance of cvclohexene over bicyclohexyl indicates that reaction 1 contributes no more than about 15% to product formation relative to the alternative mechanism (reaction 4) involving the excited state of cyclohexane (C₆H₁₂*) produced by neutralization of $C_6H_{12}^{\bullet+}$. If this excited state yields products only by dissociating to H₂ and cyclohexane, reaction 1 can be shown to account for 15% of the ions. If reaction 1 does not occur, the products can be accounted for if 15% of the neutralizations of $C_6H_{12}^{*+}$ give H^{*} and cyclohexyl radical instead of H₂ and cyclohexene. Determination of the products of single-photon excitation and ionization of cyclohexane⁶ showed that at least 20% of the chemistry for energies above the ionization threshold results in H[•] + cyclohexyl, but the results do not allow one to distinguish between the two alternative pathways for producing these products.

Note that reaction 1 must be very rapid to compete with geminate recombination (reaction 4), most of which has occurred in 0.1 ns; the total geminate recombination by reactions 2 and 4 accounts for more than 98% of the ions.

In our study of conductivity induced in cyclohexane by laser pulses,² the high-mobility cation of cyclohexane was observed and proposed to be formed by reaction 1. From the latter results, a limit was set on the fraction of the ions escaping geminate recombination which had high mobility (i.e., which were $C_6H_{13}^+$), the value being ≤ 0.35 . Comparison of this with the upper limit value of about 0.15 that can be derived from the results on product formation given here leads to the conclusion that either reaction 1 does not proceed rapidly enough to compete effectively with geminate recombination, or the fraction of escaped ions having high mobility is well below the upper limit of 0.35 cited above. (As we have discussed,² the latter



Figure 3. Log-log plot of product quantum yields (per two photons) vs incident intensity for the 248 nm photolysis of cyclohexane.

value was considered to be an upper limit because it is based on the mobility of the high-mobility ion determined by assuming that all positive ions produced in the radiolysis of cyclohexane have high mobility).

Figure 3 shows the quantum yields of the products expressed as the number of molecules per each two photons absorbed in biphotonic processes. The number of photons absorbed in biphotonic processes was obtained from the incident intensity and our previously measured "efficiency" for the biphotonic process.² The fact that the quantum yield of H₂ is less than unity is difficult to explain, because every ionization is expected to yield at least one H₂. Apart from the possibility that experimental errors are responsible, two other possible explanations are that (1) there is an inefficiency whereby the energy of two photons absorbed by a cyclohexane molecule does not give either H₂ or H atoms about 40% of the time or (2) reaction 1 has an inherent inefficiency in leading to products. The latter could be caused by a cage recombination between H[•] from neutralization of $C_6H_{13}^+$ and its accompanying $C_6H_{11}^{\bullet}$.

Cyclohexane Containing Solutes. Upon addition of an aromatic solute, the solute is ionized by consecutive absorption of two photons.^{1,2} Figure 4 shows the intensity variation of the yields per pulse of H₂, cyclohexene, and bicyclohexyl for solutions containing 5×10^{-5} M anthracene and 1×10^{-4} M biphenyl. The lines shown have slopes of 2. Within the experimental scatter, the product yields can be seen to have slopes ≤ 2 .

Figure 5 shows the dependence of the yield of H_2 on the concentrations of the two aromatic solutes. For both solutes the yield of hydrogen increases upon addition of the solute. These results can be qualitatively explained on the basis of parameters previously used to describe the conductivity signals observed in neat cyclohexane and cyclohexane/anthracene solutions,² and the mechanisms discussed below. However, the larger increase in H_2 yield in the case of biphenyl or acenaphthene is not understood.

Table 1 compares yields of products from solutions with the yields from neat cyclohexane. These are not quantum yields but are the yields for a given incident pulse. Clearly, the yields increase when an aromatic solute is added. This occurs despite the fact that the absorption of light by cyclohexane decreases



Figure 4. Log-log plot of the intensity variation of product yields in micromoles per pulse for the 248 nm photolysis of cyclohexane containing 5×10^{-5} M anthracene (solid points) and 1×10^{-4} M biphenyl (open points). The squares are for H₂, the triangles for cyclohexene, and the circles for bicyclohexyl.



Figure 5. H_2 yields as a function concentration of anthracene or biphenyl (170 mJ cm⁻², 20 pulses). The solid circles are for biphenyl, and the open circles are for anthracene. The solid square is for no solute.

markedly because of the large absorbance at 248 nm due to the solutes (the decadic molar absorption coefficients are 1.2×10^5 , 1.6×10^4 , and $1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for anthracene, biphenyl, and acenaphthene, respectively).⁷ For example, in the case of anthracene the light absorbed by the solvent is decreased to 80-85% but an increase in product formation is seen, which indicates that light absorbed by the aromatic molecule causes CH bonds in the solvent to be broken. As we have discussed previously, a likely mechanism for this is the transfer of a proton from an aromatic radical cation to cyclohexane by reaction 5

$$ArH^{\bullet+} + C_6H_{12} + h\nu_{248} \rightarrow C_6H_{13}^{+} + Ar^{\bullet}$$
 (5)

promoted by the absorption of a third photon.² The results on

the intensity dependence of the conductivity signal from the high-mobility cation in cyclohexane are in accord with this reaction if $C_6H_{13}^+$ is the high-mobility ion; furthermore, the conductivity results indicate that absorption of a photon by ArH^{*+} is necessary to cause the reaction.² The product measurements vs intensity given in Figure 4 do not show evidence of absorption of a third photon by ArH^{*+}, which would give a slope of 3 if the product were exclusively from reaction 5. The explanation for this is most likely that the experimental measurements could not be carried out to a low enough intensity range; computer simulations using the methods described earlier² indicate that the region of slope >2 would not be reached unless intensities below 10 mJ cm⁻² were used.

Whether the product spectra given in Table 1 for solutes in cyclohexane can be explained on the basis of light absorbed in the solvent and the occurrence of reaction 5 is an important point. As for neat cyclohexane, the yield of hydrogen should equal the sum of the cyclohexene and bicyclohexyl yields if no cyclohexyl radical is converted to other products. Within experimental error this holds for the anthracene results. For biphenyl and acenaphthene, the deficit of hydrocarbon products can be explained on the basis of cyclohexanol and cyclohexanone observed, apparently resulting from residual oxygen which reacts with part of the cyclohexyl radicals.

Using results on anthracene from our previous work,² we know that 1×10^{-4} M anthracene decreases the light absorption by the solvent by about 82%. The products from the solvent were estimated on this basis, using the yields from neat cyclohexane in Table 1. Yields were simulated using a simple spread sheet calculation to determine whether the balance of the products for 1×10^{-4} M anthracene can be accounted for by reaction 5. That $C_6H_{13}^+$ would yield H_2 and $C_6H_{11}^{\bullet}$ upon neutralization, as by reactions 2 and 3, seems reasonable, so this was assumed. The aryl radical (Ar[•]) probably abstracts H[•] from cyclohexane (reaction 6)

$$\operatorname{Ar}^{\bullet} + \operatorname{C}_{6}\operatorname{H}_{12} \to \operatorname{Ar}\operatorname{H} + \operatorname{C}_{6}\operatorname{H}_{11}^{\bullet} \tag{6}$$

with a rate constant of $\approx 1 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}$, based on the reported value for phenyl radicals of $4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 318 K.^{8,9} Therefore, abstraction is favored by orders of magnitude over radical-radical reactions of the aryl radical, based on rate constants for radical-radical reactions,⁹ and the known concentration of radicals produced per light pulse of $\sim 2 \times 10^{-6}$ M. Therefore, reaction 5 followed by reactions 2 and 3 would lead to H₂ and two cyclohexyl radicals. Note that reaction 3 predominates over the addition of H[•] to the aromatic solute, based on the observation that the rate constant ratio is expected to be only ≈ 35 in favor of the reaction with the aromatic¹⁰ and the ratio of 10^5 in the concentrations of cyclohexane/aromatic. On the basis of rate constants for radical addition to unsaturated compounds¹¹⁻¹⁴ the addition of cyclohexyl radicals to anthracene should be a few orders of magnitude slower than homogeneous radical recombination under the conditions of our experiment, where $[C_6H_{11}] \sim 2 \times 10^{-6}$ M. Therefore, in the absence of the effects discussed below, all H[•] should produce H₂ by abstraction, and likewise, all aryl radical should result in C₆H₁₁. The yields calculated on this basis show unequivocally that the cyclohexene and bicyclohexyl yields should be much more nearly equal than is observed experimentally. For the calculated yields to equal the experimental yields, a cage reaction between aryl and cyclohexyl resulting from reaction 5 followed by reactions 2 and 3 is required. Seventy percent of the reaction is required to be in the cage, with 94% of that giving cyclohexene. Experimental evidence consistent with the occurrence of reaction between the aryl and cyclohexyl radicals is that cyclohexylnaphthalene was observed in analogous experiments on cyclohexane/naphthalene solutions.⁴ Such a reaction would have to be a "cage" reaction unless the "escaped" aryl radical does not always abstract a hydrogen atom from cyclohexane.

Alternative explanations have been considered. Reaction 5 followed by reactions 2, 3, and 6 result in H_2 and two cyclohexyl radicals, but homolysis of ArH to Ar^{*} and H^{*} would also, and would therefore be equivalent in the mechanism given above. However, homolysis is ruled out by results on deuterated anthracene in cyclohexane, where HD was determined to account for only 1.5% of the total hydrogen.⁴ Another possibility is that both reaction 5 and charge transfer to cyclohexane from excited ArH^{+•} (reaction 7)

$$ArH^{\bullet+} + C_6H_{12} + h\nu_{248} \rightarrow C_6H_{12}^{\bullet+} + ArH$$
 (7)

occur. The $C_6H_{12}^{\bullet+}$ produced from the charge transfer would presumably give the same ratios of products as observed for neat cyclohexane. "Cage" reaction is still needed to produce correspondence with the experimental results, but the parameters describing the cage reaction are different. The charge-transfer process and reaction 5 are required to be equally important, and 55% of the aryl, cyclohexyl radical pairs must undergo cage reaction, with 80% of the cage reaction yielding cyclohexene.

Therefore, reaction of cyclohexyl with aryl, and the predominance of disproportionation in this reaction are required by either of the two likely mechanisms. Significantly, either mechanism requires participation of reaction 5, the transfer of a proton from ArH⁺⁺ to cylcohexane. This corroborates evidence for reaction 5 from studies using deuterated anthracene ($C_{14}D_{10}$), where only 1.5% of the hydrogen was HD, and where $C_{14}D_9H$ was a major product.⁴

Summary

The major products from the biphotonic ionization of neat cyclohexane by 248 nm light are H₂, cyclohexene, and bicyclohexyl. The fact that cyclohexene and hydrogen are about an order of magnitude more important than bicyclohexyl is shown on the basis of a plausible mechanism to indicate that no more than about 15% of the ionization processes result in C_6H_{13} +. When aromatic solutes are added to cyclohexane, the product yields increase despite the marked reduction in the light absorbed by the solvent. Analysis of the results indicates significant participation of proton transfer from excited aromatic radical cations to cyclohexane.

The product determinations reported here are not by themselves sufficient to unambiguously determine the reaction mechanism and processes involved in multiphoton ionization and radiolysis of alkane liquids. However, the extensive body of results from this laboratory and elsewhere can best be explained by requiring significant participation of ion-molecule processes exemplified by reactions 1 and 5. This includes observations of high-mobility solvent ions under a variety of experimental conditions, results of picosecond pulse radiolysis studies, and nanosecond magnetic resonance studies; a summary of these studies has been given.¹⁵ Although some quantitative details are still elusive, a mechanism based on reactions 1 and 5 provides the best explanation for a wide range of observations.

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