

Stereospecific (Conrotatory) Photochemical Ring Opening of Alkylcyclobutenes in the Gas Phase and in Solution. Ring Opening from the Rydberg Excited State or by Hot Ground State Reaction?

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The photochemistry of 1,2-dimethylcyclobutene and *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene has been studied in the gas phase (1 atm; SF₆ buffer) and in hydrocarbon solvents with 193-, 214-, and 228-nm light sources. The major products are the isomeric dienes from electrocyclic ring opening and 2-butyne + alkene (ethylene or *E/Z*-2-butene) due to formal [2+2]-cycloreversion. The total yields of dienes relative to 2-butyne are generally higher in the gas phase than in solution but decrease with increasing excitation wavelength under both sets of conditions. In the case of *cis*-1,2,3,4-tetramethylcyclobutene, 228-nm photolysis results in the *stereospecific* formation of *E,Z*-3,4-dimethyl-2,4-hexadiene—the isomer corresponding to ring opening by the thermally allowed (*conrotatory*) electrocyclic pathway—in both the gas phase and solution. All three diene isomers are obtained upon 228-nm photolysis of *trans*-1,2,3,4-tetramethylcyclobutene, but control experiments suggest that the thermally allowed isomers (*E,E*- and *Z,Z*-3,4-dimethyl-2,3-hexadiene) are probably the primary products in this case as well. The results are consistent with cycloreversion resulting from excitation of the low-lying $\pi, R(3s)$ singlet state and with ring opening proceeding by at least two different mechanisms depending on excitation wavelength. The first, which dominates at short wavelengths, is thought to involve direct reaction of the second excited singlet (π, π^*) state of the cyclobutene. The second mechanism, which dominates at long wavelengths, is proposed to ensue either directly from the lowest energy (Rydberg) state or from upper vibrational levels of the ground state, populated by internal conversion from this excited state.

Introduction

The direct irradiation of alkylcyclobutenes in hydrocarbon solvents results in competing electrocyclic ring opening and formal [2+2]-cycloreversion.¹ Ring opening proceeds nonstereospecifically, and it has been shown that in certain cases, the mixtures of isomeric dienes produced can be accounted for by a mechanism involving exclusive *adiabatic* disrotatory ring opening, with internal conversion to the ground-state potential energy surface occurring by *cis,trans*-isomerization *after* the diene is formed.^{2–4} In contrast, the formal [2+2]-cycloreversion reaction proceeds stereospecifically, yielding (in addition to the corresponding alkyne) a single alkene isomer whose stereochemistry corresponds to that at C3–C4 of the cyclobutene precursor.^{5–7} Despite the high degree of stereoselectivity of the process, there is evidence to suggest that it proceeds nonconcertedly via a cyclopropylmethylene intermediate, perhaps in competition with the pericyclic cycloreversion pathway.⁸

There are at least two excited singlet states accessible in alkylcyclobutenes by direct irradiation in the 185–

230-nm spectral range, and both have been proposed to contribute directly to the photochemistry.^{7,9} The UV spectra of 1,2-disubstituted alkylcyclobutenes are typical of tetrasubstituted alkenes, showing a prominent (π, π^*) absorption band in the 185–195-nm range and, in the gas phase, a finely structured band at longer wavelengths (200–230 nm) due to $\pi, R(3s)$ absorptions.^{7,10–12} In condensed phases, the position of the Rydberg absorption band shifts to slightly shorter wavelengths, the fine structure is absent, and the band is substantially reduced in intensity. This character, and the fact that its position correlates with the vertical π -ionization potential of the alkene, are characteristic of Rydberg absorptions.¹²

The relative contributions of the π, π^* and $\pi, R(3s)$ states to the photochemistry of aliphatic alkenes has been extensively investigated in both the gas and solution phases.^{13–16} There appears to be general agreement that the valence (π, π^*) state is responsible for direct *cis,trans*-photoisomerization, whereas the Rydberg state is responsible for the formation of skeletal rearrangement products, involving carbene intermediates resulting from

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initial [1,2]-migration of a vinylic substituent.^{15,16} Long-wavelength irradiation of tetrasubstituted alkenes in hydroxylic media leads to the formation of alcohols or ethers, consistent with nucleophilic trapping of a species with the radical cation character expected of alkene $\pi, R(3s)$ Rydbergs.^{17,18}

In principle, the Rydberg state could provide an alternate pathway to ring opening in cyclobutene derivatives and account for the nonstereospecificity of the reaction if the stereochemistry differed from that of the π, π^* process. Cyclobutene radical cations are known to undergo thermally activated ring opening,^{19–22} and there is one example²³ that suggests that the reaction proceeds with the conrotatory stereochemistry that is predicted by theory.^{24–26} In two previous papers, we tentatively ruled out this possibility on the basis of correlations of the gas- and solution-phase electronic spectra of two different series of cyclobutene derivatives with product distributions obtained from photolyses in solution as a function of substituent and excitation wavelength.^{7,9} The yields of cycloreversion relative to ring-opening products were found to increase with excitation wavelength between 185 nm (where π, π^* absorption predominates) and 214 nm (where $\pi, R(3s)$ absorption predominates), with little variation in isomeric diene distribution. This is consistent with electrocyclic ring opening arising predominantly from the π, π^* state and [2+2]-cycloreversion from the Rydberg excited state. Clearly, if these assignments are correct, then it might be expected that *selective* excitation of the Rydberg absorption band should lead only to cycloreversion. Such an experiment should be possible with 1,2-dialkylcyclobutenes, whose lowest energy absorption band extends to beyond 230 nm and is particularly prominent in the gas phase.

Perhaps surprisingly, the gas-phase photochemistry of cyclobutene has not been extensively studied.^{27,28} Vacuum-UV (106–147 nm) photolysis of cyclobutene itself at <10 Torr total pressure leads mainly to fragmentation; small amounts of 1,3-butadiene are also formed but have been shown to be due to reaction of hydrogen atoms with the ground-state precursor.²⁸ The only other gas-phase study reported is from Haller and Srinivasan, who examined the mercury-sensitized photolysis of the molecule.²⁷ The photochemistry under these conditions bears little resemblance to that obtained in solution.²⁹

In this paper, we report the results of a study of the photochemistry of three simple monocyclic alkylcyclobutene derivatives in the gas phase at atmospheric pressure, using monochromatic light sources of wave-

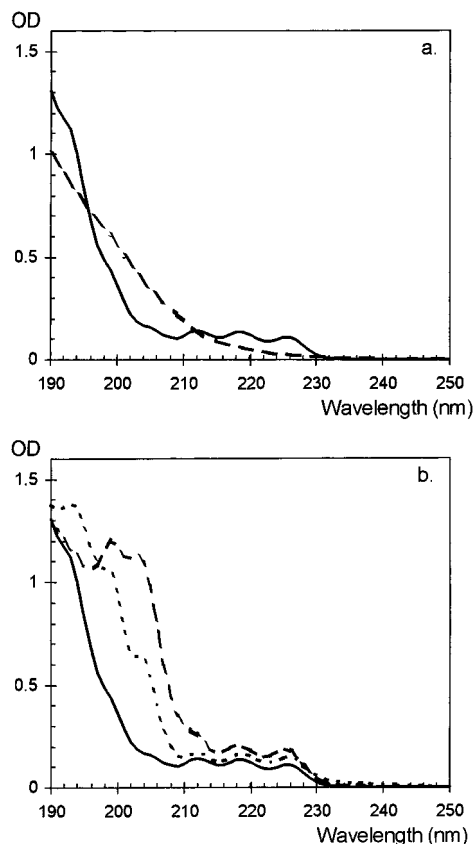
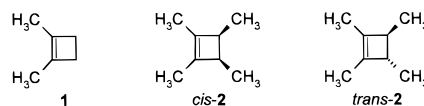


Figure 1. UV absorption spectra of (a) **1** in pentane solution (---) and in the gas phase (—) at 25 °C and (b) **1** (—), *c*-**2** (---), and *t*-**2** (···) in the gas phase (SF₆ buffer; 1 atm total pressure).

length 193, 214, and 228 nm. The compounds chosen for this investigation, 1,2-dimethyl- (**1**), *cis*-1,2,3,4-tetramethyl- (*cis*-**2**), and *trans*-1,2,3,4-tetramethylcyclobutene (*trans*-**2**), have all been studied previously in solution with 193- and 214-nm light sources.^{7,30} In the gas phase,



all three compounds possess low-lying $\pi, R(3s)$ states, which can be selectively populated by direct irradiation with 228-nm light. Solution-phase experiments with the three light sources have also been carried out to allow a full comparison of the wavelength effects on the photochemistry of these compounds in both the gas phase and solution under standard sets of conditions.

Results

The UV absorption spectra of **1** in the gas phase (1 atm SF₆) and in pentane solution are shown in Figure 1a. Figure 1b shows the gas-phase spectra of all three cyclobutenes recorded under the same conditions (1 atm; SF₆ buffer). The spectra of *cis*- and *trans*-**2** are indistinguishable from those reported previously at lower total pressures.⁷ All three spectra exhibit a weak, structured band at long wavelengths that is assignable to $\pi, R(3s)$ absorptions and a more intense band at shorter wave-

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Table 1. Product Yields from Photolysis of 1,2-Dimethylcyclobutene (1) and *cis*- and *trans*-1,2,3,4-Tetramethylcyclobutene (*cis*- and *trans*-2) in the Gas Phase (1 atm SF₆) and as Deoxygenated 0.05 M Solutions in Isooctane (1) or Hexane (2) at 25 °C^a

compd	λ_{ex} (nm)	gas phase				hydrocarbon solution			
		4	3	4	3				
1	193	28 ± 2	72 ± 5	43 ± 3	57 ± 4				
	214	31 ± 4	64 ± 4	50 ± 1	45 ± 3				
	228	32 ± 1	62 ± 3	56 ± 4	44 ± 4				

compd	λ_{ex} (nm)	gas phase				hydrocarbon solution			
		4	<i>EE</i> -6	<i>EZ</i> -6	<i>ZZ</i> -6	4	<i>EE</i> -6	<i>EZ</i> -6	<i>ZZ</i> -6
<i>cis</i> -2	193	39 ± 2	20 ± 2	41 ± 2	<1	34 ± 2	40 ± 2	25 ± 2	<1
	214	50 ± 1	7.0 ± 0.5	42 ± 1	<1	48 ± 2	21 ± 2	31 ± 2	<1
	228	55 ± 3	<1	45 ± 2	<1	59 ± 7	<1	40 ± 2	<1
<i>trans</i> -2	193 ^b	39 ± 1	41 ± 2	13 ± 2	7 ± 1	40 ± 1	21 ± 2	34 ± 2	4 ± 1
	214 ^b	43 ± 2	38 ± 2	10 ± 2	9 ± 1	50 ± 2	14 ± 2	29 ± 2	7.5 ± 0.5
	228 ^b	57 ± 3	22 ± 2	12 ± 2	8 ± 1	76 ± 4 ^c	3 ± 1 ^c	13 ± 2 ^c	8 ± 2 ^c

^a Based on triplicate determinations of relative product yields at maximum conversion. All solution-phase photolyses employed 0.05 M solutions and were carried to a maximum conversion of 5–8%, unless otherwise noted. ^b Maximum conversion 0.7–1.5%. ^c Concentration = 0.15 M.

Table 2. Ring-Opening/Cycloreversion Ratios (3(6)/4) and Isomeric Diene Distributions from Photolysis of 1 and 2 with 193–228-nm Light in the Gas Phase (1 atm SF₆) and as Deoxygenated 0.05 M Solutions in Isooctane or Hexane^a

compd	λ_{ex} (nm)	gas phase			hydrocarbon solution		
		3(6)/4	<i>EE</i> : <i>EZ</i> : <i>ZZ</i>	therm/photo ^b	3(6)/4	<i>EE</i> : <i>EZ</i> : <i>ZZ</i>	therm/photo ^b
1	193	3.0			1.3		
	214	2.4			0.92		
	228	2.0			0.79		
<i>cis</i> -2	193	1.6	1:2:0	2.0	1.9	1.6:1:0	0.63
	214	0.90	1:3.3:0 ^c	3.3	1.1 ^c	1.1:1.0:0 ^c	1.0
	228	0.82	<1:>20:0	>20	0.69	<1:>20:0	>20
<i>trans</i> -2	193	1.6	6:2:1	3.5	1.5	5.2:8.5:1	0.74
	214	1.6	4.3:1:1.1	5.4	0.80	2.2:4.2:1	0.76
	228	1.3	2.4:1:1 ^c	3.0	0.25 ^c	1:2.6:2.3 ^c	1.3
pss ^d	228		1:7:2			1:7.1:4.4	

^a Photolyses of **1** were carried out in isooctane solution, whereas those of *cis*- and *trans*-2 were carried out in hexane solution. ^b Therm/photo represents the ratio of thermally allowed to photochemically allowed diene isomers, i.e., [*EZ*-6]/([*EE*-6] + [*ZZ*-6]) from photolysis of *cis*-2 and the inverse for the *trans* isomer. ^c From the intercepts of plots of product ratio ([6]/[4], [*EE*-6]/[*EZ*-6] and [*ZZ*-6]/[*EZ*-6]) vs conversion, from photolysis of a 0.15 M hexane solution of *trans*-2. ^d The photostationary state for direct *E,Z*-photoisomerization, established starting from pure *E,E*-6 and pure *E,Z*-6.

lengths assignable to π, π^* absorptions. The long wavelength bands in the three compounds are reduced in intensity, devoid of fine structure, and shifted to shorter wavelengths in the solution-phase spectra, consistent with the gas-phase $\pi, R(3s)$ assignment (see Figure 1a and ref 7).

Direct irradiation of samples of **1** and **2** (partial pressure \approx 200 Torr) in an SF₆ buffer (total pressure = 760 Torr) was carried out with an (unfocused) ArF excimer laser (193 nm) and zinc and cadmium resonance lamps (214 and 228 nm, respectively). The product distributions did not vary with the laser intensity so long as it was kept at modest levels, but much higher intensities resulted in increased yields of dienes relative to **4**.

The photolyzates were monitored as a function of photolysis time by capillary gas chromatography (GC), and products were identified by co-injection of the photolyzates with authentic samples. Photolysis of the three compounds gave rise to the products shown in eqs 1–3 at conversions below \sim 8%; no others could be detected in yields greater than ca. 5% under our analytical conditions. The three compounds were also photolyzed as deoxygenated 0.05 M solutions in isooctane (**1**) or hexane (**2**) with the three light sources.

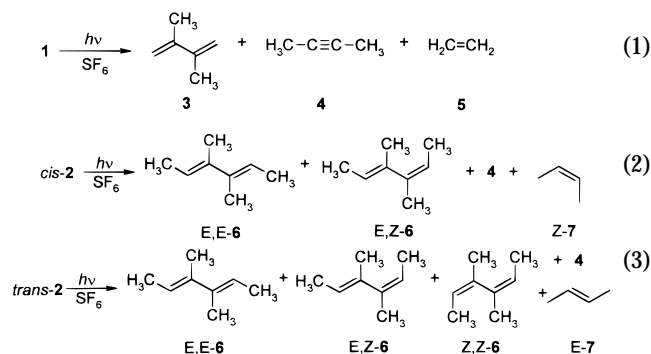


Table 1 contains percentage yields of products, determined by triplicate GC analysis of the product mixtures at maximum conversion, with corrections for differences in GC response factors. Table 2 contains various product ratios, calculated from the slopes of concentration vs conversion plots. These generally showed good linearity up to conversions of \sim 6%. In a few cases (e.g., the 228-nm photolyses of *trans*-2), plots of the isomeric diene yields vs conversion showed mild curvature, suggestive of secondary photolysis effects. The data were thus also plotted in the form of product ratios versus conversion to magnify any systematic variations in product distribution with photolysis time. Plots of [3]/[4] vs conversion

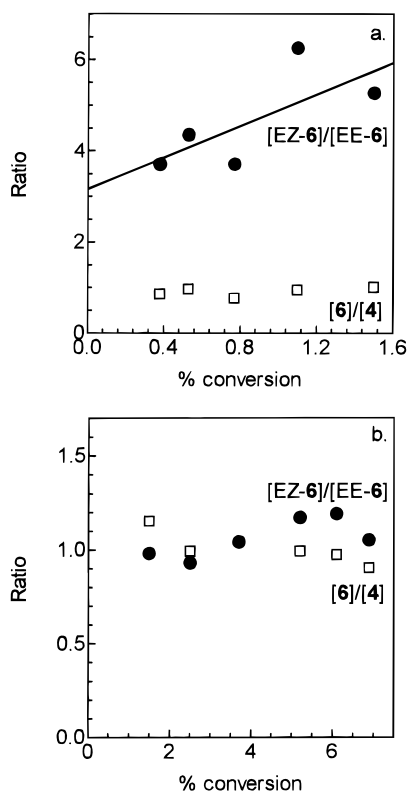


Figure 2. Plots of product ratios versus time for the 214-nm photolysis of *cis*-1,2,3,4-tetramethylcyclobutene (*cis*-2) in (a) the gas phase (1 atm SF₆) and (b) hexane solution (0.05 M) at 25 °C. The quantity [6]/[4] is the total yield of dienes (all isomers) relative to that of 2-butyne (4).

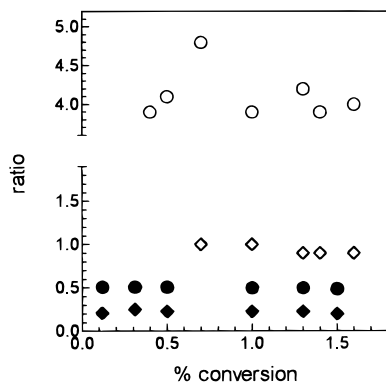


Figure 3. Plots of isomeric diene ratios [EE-6]/[EZ-6] (circles) and [ZZ-6]/[EZ-6] (diamonds) versus % conversion for the 214-nm photolysis of *trans*-1,2,3,4-tetramethylcyclobutene (*trans*-2) in the gas phase (open symbols) and hexane solution (solid symbols) at 25 °C.

from the photolysis of **1** were linear, with slopes indistinguishable from zero for all three excitation wavelengths in both gas and solution phases. The same was true of the plots of the total yields of dienes relative to 2-butyne ([6]/[4], where [6] = [EE-6] + [EZ-6] + [ZZ-6]) vs conversion for photolysis of *cis*- and *trans*-2 at the three excitation wavelengths in the two phases. The zero slopes of these plots suggest that the total product yields are unperturbed by secondary photolysis effects in these cases. However, plots of the individual diene ratios had nonzero slopes for the photolysis of both *cis*- and *trans*-2 in the gas phase at 214 nm (Figures 2 and 3) and for the 228-nm photolyses of *trans*-2 in both the gas and solution

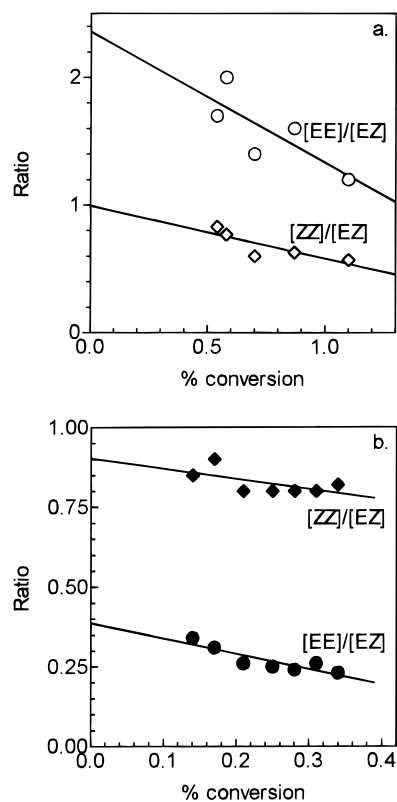


Figure 4. Plots of isomeric diene ratios versus time for the 228-nm photolysis of *trans*-1,2,3,4-tetramethylcyclobutene (*trans*-2) in (a) the gas phase (1 atm SF₆) and (b) hexane solution (0.05 M) at 25 °C.

phases (Figure 4). In these cases, the primary product ratios were taken as the intercepts of these plots. The product distributions obtained from photolysis of **1** and **2** in pentane solution with 193- and 214-nm light (see Table 1) agree fairly well with those published by us in earlier studies of these compounds.^{7,30}

For example, Figure 2 shows plots of [6]/[4] and [EZ-6]/[EE-6] vs conversion for the 214-nm photolyses of *cis*-2 in the gas and solution phases (ZZ-6 was not formed in detectable yields at either 214 or 228 nm, at conversions < 5%). Gas- and solution-phase photolysis of *cis*-2 at 228 nm led to the formation of only **4** and *E,Z*-6 at conversions up to ~8%. Plots of [EE-6]/[EZ-6] and [ZZ-6]/[EZ-6] vs conversion from the photolyses of *trans*-2 in the two phases at 214 and 228 nm are shown in Figures 3 and 4, respectively.

The product yields and ratios listed in Tables 1 and 2 for the 228-nm photolysis of *trans*-2 in hexane were actually determined using a deoxygenated 0.15 M solution of the cyclobutene, with monitoring of the photolyzate over the 0.2–0.8% conversion range. Photolysis of this compound under the same conditions as used for all of the other experiments summarized in the Tables (i.e., 0.05 M *trans*-2), but with monitoring over the 2–7% conversion range, afforded product ratios that varied more substantially with conversion; the values extrapolated to 0% conversion are [6]/[4] = 0.32 and *EE:EZ:ZZ*-6 = 1:3.2:2.1.

Table 2 also contains the photostationary state compositions for direct irradiation of **6** with 228-nm light, which were determined under the same conditions as those employed above for photolysis of the cyclobutenes. These ratios were determined by exhaustive photolysis

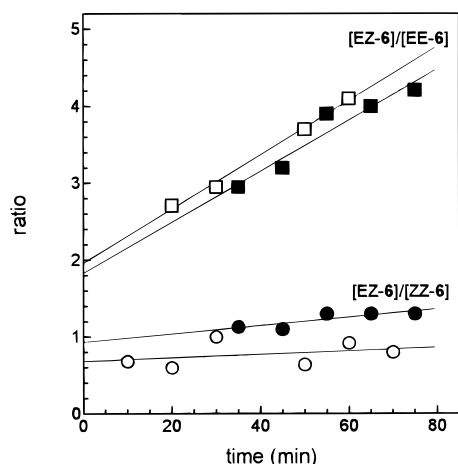
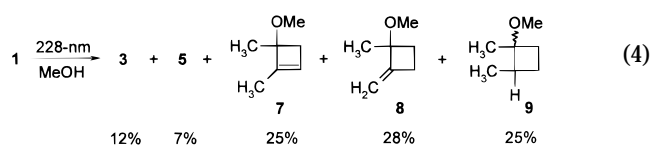


Figure 5. Isomeric diene ratios from the 228-nm photolysis of *t*-**2** in pentane solution (filled symbols) and from the 228-nm photolysis of **1** to which a 1:1 solution of *E,E*- and *Z,Z*-**6** is slowly added (open symbols).

of samples of *E,E*- and *E,Z*-**6**, which led to the formation of complex mixtures of *cis*- and *trans*-**2** and other isomeric products but common mixtures of *E,E*-, *E,Z*-, and *Z,Z*-**6**.

A control experiment was performed, in which a hexane solution of **1** (0.15 M) was photolyzed with the 228-nm light source while a 1:1 mixture of *E,E*- and *Z,Z*-**6** (total concentration \approx 0.02 M) was introduced via a syringe pump, at a rate corresponding roughly to the total rate of diene formation in the photolysis of *trans*-**2** under the same conditions. GC analysis of aliquots of the photolysis mixture as a function of irradiation time showed *E,Z*-**6** to be formed efficiently under these conditions, even at the shortest irradiation period monitored; Figure 5 shows plots of *E,Z*-/*E,E*- and *E,Z*-/*Z,Z*-**6** versus photolysis time for this experiment, overlaid on the corresponding plots from the photolysis of the 0.15 M solution of *trans*-**2**.

Irradiation of a deoxygenated 0.05 M solution of **1** in methanol with the 228-nm light source resulted in the formation of three major products in approximately equal yields, in addition to small amounts of **3** and **5** (**4** coelutes with the solvent under our GC conditions, so its formation in this experiment can only be inferred from the fact that **5** is formed). The three major products had similar retention times under our GC conditions, so that baseline resolution could not be achieved even by capillary GC. Consequently, they could only be tentatively identified as **7**–**9** on the basis of ^1H NMR and mass spectral data recorded on enriched mixtures (see eq 4). The yields of



7–**9** were reduced to ca. 40% of the total, and those of **3** and **5** increased to 36% and \sim 20%, respectively, when a similar solution was irradiated at 214 nm. Equation 4 shows the results of the 228-nm experiment; product yields were estimated after \sim 20% conversion by GC.

Discussion

The gas- and solution-phase UV absorption spectra of 1,2-dimethylcyclobutene (**1**; Figure 1) and the differences

between them are typical of the UV spectra of tetraalkyl-substituted alkenes.^{10–12} The gas-phase spectrum shows the structured long wavelength absorption band, with vibronic spacings on the order of 1400–1500 cm^{-1} , which is typical of alkene $\pi, \text{R}(3\text{s})$ absorptions,¹² along with a more intense band below 200 nm which can be assigned to the valence (π, π^*) absorption. The intensity and fine structure associated with the long wavelength absorption band is reduced in the solution-phase spectrum, and the absorption is shifted to shorter wavelengths, consistent with the Rydberg assignment in the gas-phase spectrum. The absorption spectra of *cis*- and *trans*-**2** both show a set of $\pi, \text{R}(3\text{s})$ absorptions similar to that of **1** but more pronounced fine structure in (or superimposed on) the intense π, π^* absorption at shorter wavelengths. This structure manifests itself as three bands at 193, 199, and 203 nm (i.e., vibronic spacings on the order of 1000–1200 cm^{-1}), of which the latter two are considerably more prominent in the spectrum of the *trans* isomer than in that of the *cis*.⁷ We previously assigned these to $\pi, \text{R}(3\text{p})$ absorptions, primarily on the basis of the fact that the fine structure is washed out in the solution-phase spectra of the two compounds.

In all three cases, there is a marked trend toward increased yields of cycloreversion relative to ring-opening products with increasing excitation wavelength, in both the gas phase and solution. This is consistent with the conclusion that cycloreversion arises predominantly from the lower energy Rydberg state, whereas ring opening results mainly from the π, π^* state.⁷ However, the observation of significant yields of dienes in the 228-nm photolyses, where there is insufficient energy to populate the π, π^* state directly, clearly indicates that there exists a second mechanism for ring opening that involves the lower energy excited state. This second mechanism is generally more important in the gas phase than in solution, and furthermore, it has significantly different stereochemical characteristics than that which dominates at shorter excitation wavelengths. This is most evident from the results of photolysis of *cis*-**2** with 228-nm light, where the *thermally allowed* diene isomer (*E,Z*-**6**) is formed *stereospecifically* in both the gas phase and solution. In contrast, photolysis of *trans*-**2** at the same wavelength produces all three diene isomers, in distributions which only slightly favor the *thermally allowed* diene isomers (*EE*- and *ZZ*-**6**) relative to the other. In this case, the main effect of increasing excitation wavelength is a trend toward increased yields of the *Z,Z*-diene relative to the *E,E*-isomer, and it is more pronounced in solution than in the gas phase.

Because the dienes absorb considerably more strongly than the cyclobutenes at 228 nm in solution, the contribution of secondary photolysis effects to the observed distributions of diene isomers from photolysis of **2** requires careful evaluation. Such effects are clearly unimportant with *cis*-**2**, which yields only a single diene isomer within the limits of our detection method over the 0.4–7% conversion range. They are a cause of real concern in the case of *trans*-**2**, however, for which the observed diene distribution changes with conversion and approaches the photostationary state composition at this wavelength (*EE*/*EZ*/*ZZ* = 1:7.1:4.4). If one assumes that the primary diene distribution from photolysis of *trans*-**2** at 228 nm is analogous to that from *cis*-**2** (i.e., that it consists only of the *thermally allowed* (*EE*- and *ZZ*-) diene isomers), then it is clear that greater problems from

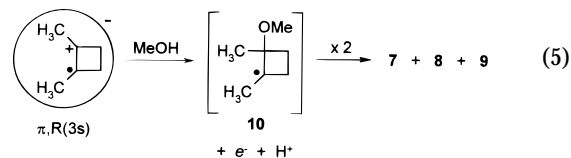
secondary photolysis are to be expected for the *trans*-isomer. This follows from consideration of the diene 228-nm pss, which shows that the *E,E*-diene isomer is the most sensitive to secondary photolysis at this wavelength, whereas the *E,Z*-diene is the least sensitive. It should be noted that although these effects might skew the diene isomer distribution away from its true value, they should have little effect on the cycloreversion/ring-opening ratio (i.e., $[4]/[EE+EZ+ZZ-6]$), because the quantum yields for ring closure of these dienes are considerably lower than those for *cis,trans*-photoisomerization. Thus, the 2-butene/diene ratios from photolysis of both isomers of **2** can be safely assumed to be close to their "true" values. Further evidence for this is obtained from the fact that there is no detectable formation of *trans*-**2** from *cis*-**2**, and vice versa, in the photolyses at any of the three wavelengths.

The syringe pump experiment, in which a 1:1 mixture of *EE*- and *ZZ*-**6** was introduced into a continuously photolyzed solution of **1** (0.15 M) at a rate corresponding roughly to that of total diene formation in the 228-nm photolysis of *trans*-**2**, was carried out to quantify the importance of secondary photolysis effects in the photolysis of this compound. GC analyses of the photolyzate at various time intervals during photolysis (Figure 5) show that even after the shortest irradiation period (corresponding to ca. 0.2% conversion of *trans*-**2** in the original experiment), the *E,Z*-diene comprises slightly more than 50% of the distribution of the isomers of **6**. The relative yield of *E,Z*-**6** continues to increase with continued photolysis, in parallel fashion to that in the original experiment. The close correspondence between the plots of diene–isomer ratio vs time from the original photolysis of 0.15 M *trans*-**2** and those from the control experiment strongly suggests that the primary diene distribution from photolysis of *trans*-**2** in hexane at 228 nm is close to a 1:1 mixture of *E,E*- and *Z,Z*-**6**, with relatively little of the *E,Z*-isomer present. We thus conclude that photolysis of both *cis*- and *trans*-**2** with the 228-nm light source results in the predominant (or possibly exclusive) formation of the thermally allowed diene isomer(s) as the primary products.

The present results indicate that both the π,π^* and $\pi,R(3s)$ excited states of alkylcyclobutenes are responsible for ring opening. Most significantly, it is clear that the lower energy state reacts via a mechanism that results in the preferential formation of the thermally allowed diene isomer(s). The effect is particularly pronounced in the gas phase, where the relative yields of dienes are significantly higher than in solution. There are at least two possible explanations for these results.

The first explanation is that ring opening proceeds from the Rydberg state as a true excited-state process but with different stereochemical characteristics than π,π^* -state ring opening. This might be consistent with the radical cation character of alkene $\pi,R(3s)$ Rydberg states¹³ and the fact that cyclobutene radical cations are predicted by theory to undergo ring opening with conrotatory stereochemistry.^{24–26} Evidence that the lowest Rydberg state of **1** possesses the same general electronic character as those of simpler tetrasubstituted alkenes is provided by the results of 228-nm photolysis of the compound in methanol solution, where the major products are the methyl ethers **7–9**. Ring-opening and cycloreversion products (**3–5**) are formed in only minor amounts, and the rates of their formation appear to be

substantially lower than in isoctane solution. This is consistent with a concomitant reduction in the quantum yields for cycloreversion and ring opening as a result of competitive quenching of the Rydberg excited state by the solvent. Compounds **7–9** are the products expected from disproportionation of the free radical formed by nucleophilic trapping of the Rydberg state by the solvent (eq 5). Analogous results have been reported for other



tetrasubstituted alkenes by Kropp and co-workers.³¹ Photolysis of **1** in methanol with 214-nm light, where both the π,π^* and $\pi,R(3s)$ states are populated, results in substantially lower yields of **7–9** relative to **3**. It is not clear why **7–9** appear to be formed in roughly equal yields; this mechanism would predict that the yield of **9** should be equal to the sum of those of **7** and **8**.

Alkylcyclobutene radical cations have been shown to undergo fast thermal ring opening when generated in the gas phase²⁰ but *not* in solution^{21,32} or other condensed phases.^{22,33} These results are consistent with the theoretical indication that the process requires thermal activation.²⁴ If this requirement holds as well for ring opening in the $\pi,R(3s)$ Rydberg state, then this mechanism would not be expected to be a major contributor to diene formation in either the gas phase or solution under the conditions of our experiments, assuming that the intrinsic lifetimes of the $\pi,R(3s)$ states in 1,2-dialkylcyclobutenes are not longer than the value estimated for the $\pi,R(3s)$ state of 2,3-dimethyl-2-butene, estimated to be on the order of ~ 15 ps.^{34,35} It is interesting to note that a lifetime in this range requires that quenching of the Rydberg state by methanol proceed at the diffusion-controlled rate to account for the significant yields of **7–9** formed upon photolysis of **1** in methanol.

The second possibility is that the lower energy excited state is itself unreactive toward ring opening but contributes to the process by providing a pathway for internal conversion to upper vibrational levels of the ground state of the cyclobutene, from which thermal ring opening ensues. This mechanism is consistent with the increased total yields of ring opening relative to cycloreversion products in the gas phase compared to those in solution, where the solvent provides a more efficient means of vibrational relaxation than 1 atm of SF₆. The buffer gas does appear to quench higher activation energy hot ground-state processes that would be expected at much lower pressures, such as C–H and C–C bond fragmentation.³⁶ Relatively few conclusively established hot ground-state reactions exist in the solution-phase photochemistry literature, but it seems reasonable to expect that such processes might be important for

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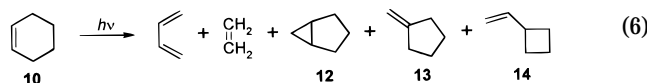
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relatively small molecules (for which collisional deactivation by the solvent is relatively slow^{37–39}), particularly when they exhibit low excited-state reactivity and possess particularly low energy pathways for reaction in the ground state. Monocyclic alkylcyclobutenes, which undergo thermal ring opening with Arrhenius activation energies in the 32–37 kcal/mol range,^{40–43} would seem to be ideal candidates in this regard.

Qualitatively, we can address the viability of this mechanism by considering cyclobutene in the context of other cycloalkenes that undergo thermal (pericyclic) reactions that differ from their excited-state reactions. Two examples are provided by cyclohexene (**10**) and norbornadiene (**11**), which undergo thermal [4+2]-cycloreversion with $E_a = 65.2$ kcal/mol⁴⁴ and 50.2 kcal/mol,⁴⁵ respectively. The photochemistry of both of these molecules has been studied extensively in the gas phase and in solution.^{46–50}

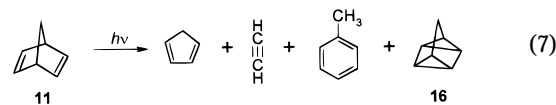
Direct irradiation of cyclohexene vapor with 185- or 214-nm light affords 1,3-butadiene, ethylene, bicyclo-[3.1.0]hexane (**12**), methylenecyclopentane (**13**), and small amounts of vinylcyclobutane (**14**) (see eq 6).^{46–49} The



major products at low pressures are butadiene and ethylene, which are formed with a quantum yield of $\Phi \approx 0.85$ at 5 Torr.⁴⁷ The quantum yield for formation of the latter two products decreases by a factor of ~ 2 with increasing pressure between 5 and 30 Torr.⁴⁶ Their formation still persists at pressures as high as 500 Torr⁴⁸ but does not occur detectably in solution-phase photolyses.⁴⁶ The process has been ascribed to a hot ground-state reaction on the basis of its pressure dependence and the fact that it proceeds with $[\pi 4s + \pi 2s]$ -stereochemistry.⁵¹ Immediately after internal conversion from the lowest excited singlet state, **10** would contain ~ 130 kcal/mol of excess thermal energy (corresponding to an effective internal temperature in excess of 2000 K³⁹), well above that corresponding to the activation barrier for ground-state [4+2]-cycloreversion ($E_a \sim 65$ kcal/mol).

The major products of photolysis (254-nm) of norbornadiene (**11**) in the gas phase are the retro-Diels–Alder products cyclopentadiene and acetylene, formed with

quantum yields ($\Phi = 0.4–0.5$) that are roughly independent of total pressure and buffer gas.⁵⁰ In solution, photolysis of **11** results in the formation of nortricyclane (**16**), as well as the three products observed in the gas phase (see eq 7). In contrast to the case of cyclohexene,

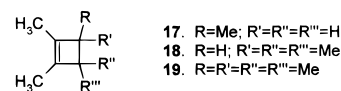


the quantum yield for cycloreversion of **11** to cyclopentadiene and acetylene is reduced by a factor of ~ 4 in solution compared to that in the gas phase, *but it is not eliminated*. In this case, thermal cycloreversion is considerably more facile ($E_a = 50.2$ kcal/mol and $\log A = 14.6$)⁴⁵ than in cyclohexene. Even though the excess thermal energy contained in the molecule after internal conversion is lower (~ 110 kcal/mol) in this case than with cyclohexene, it is evidently sufficient to allow cycloreversion to compete with collisional deactivation by the solvent.

The Arrhenius activation parameters for the thermal ring opening of **1** and **2** are in the range $E_a = 33–37$ kcal/mol ($\log A \approx 14$),^{40,41,52} and the lowest excited singlet state energies (~ 125 kcal/mol) are even higher than that of **11**. Internal energy redistribution can be expected to be somewhat more effective in **2** than in **11** because of the larger number of vibrational degrees of freedom, but as a result of the higher excited-state energy, one would still expect the vibrationally excited molecules to be formed with effective internal temperatures of at least 2000 K. Clearly, ring opening can be expected to compete quite significantly with collisional deactivation by the solvent under these conditions.

Our results suggest that the 228-nm photolysis of *trans*-**2** leads to the formation of *E,E*- and *Z,Z*-**6** in nearly equal amounts, to the exclusion of the thermally forbidden *E,Z*-isomer. Unfortunately, these results afford only a qualitative estimate of the likely primary diene isomer distribution, so we are unable to pinpoint the degree of torquoselectivity in the formation of the two isomers more precisely. The *Z,Z*-isomer is not formed in detectable yields on thermolysis of this compound at 150–200 °C,^{40,41} consistent with the Arrhenius activation energy for its formation being on the order of 5–6 kcal/mol higher than that for formation of the *E,E*-isomer.⁵³ However, because of the very high effective temperatures that are presumably involved in photochemically induced hot ground-state ring opening, one would expect to observe considerably lower torquoselectivity than would be obtained under conventional thermolytic conditions.

In a recent study of the 214-nm photolysis of the homologous series of methylated cyclobutenes **1**, **2**, and **17–19** in hydrocarbon solution, we showed that the



quantum yields for ring opening vary systematically with the degree of methyl substitution at the sp^3 carbons of the cyclobutene ring, in the manner expected if ring opening proceeds via the adiabatic, orbital symmetry-

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controlled mechanism.³⁰ It is also the trend expected if ring opening is dominated by the Rydberg-derived hot ground-state mechanism, because the rate constants for thermal ring opening of these six compounds vary in fashion similar to the quantum yields for photochemical ring opening at this excitation wavelength.

Conclusions

The results reported in this paper raise new questions regarding the origins of the nonstereospecificity of the photochemical ring opening of cyclobutene in solution. It remains obvious that there is a much greater selectivity for formation of the diene isomer(s) corresponding to orbital symmetry-allowed, disrotatory ring opening with shorter wavelength excitation, where the π, π^* state is populated. Results reported previously for several bicyclic cyclobutenes whose isomeric dienes are constrained to be in the *s-cis* conformation are quantitatively compatible with an adiabatic, purely disrotatory ring-opening mechanism,²⁻⁴ but it is now clear that this is *not* general. In monocyclic alkylcyclobutenes, the $\pi, R(3s)$ Rydberg state also contributes to ring opening, either via direct reaction with orbital symmetry characteristics identical to those of the ground-state process or by simply providing a conduit for thermal ring opening from vibrationally activated ground-state molecules. To what extent this second mechanism contributes to ring opening at shorter wavelengths, and with what degree of generality, remains to be determined.

Experimental Section

The cyclobutenes studied in this work were prepared as previously reported,³ as were authentic samples of *E,E*-, *E,Z*-, and *Z,Z*-3,4-dimethyl-2,4-hexadiene.⁵⁴ The cyclobutenes were purified to >99% purity by semipreparative gas chromatography, using stainless steel columns (20% ODPN on 80/100 Chromosorb PNAW, 0.25" \times 20' for **1**; 3.8% UCW-982 on 80/100 Supelcoport, 0.25" \times 24' for **2** and **6**). Sulfur hexafluoride (VitalAire, Inc.), methanol (Aldrich, spectrophotometric grade), cyclohexane, hexanes, and isooctane (all BDH Omnisolv) were used as received from the suppliers. Gas- and solution-phase UV absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer in 1 cm Suprasil cells. Analytical gas chromatographic separations were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 0.53 mm \times 30 m DB-1 fused silica column (Chromatographic Specialties, Inc.). FID response factors were determined for **3** and the various isomers of **6** by construction of working curves from solutions of authentic samples of the dienes.

Gas-phase samples for spectroscopy and photolysis were prepared by placing a quantity (1 μ L for spectra, 8 μ L for photolyses) of the neat cyclobutene derivative and cyclohexane (0.05 μ L) in a 1-cm Suprasil cuvette which had been flushed for ca. 5-min. with a stream of SF₆, and were sealed with rubber septa. The samples were allowed to vaporize completely before beginning the experiments. Solution-phase samples in

hexanes or isooctane contained the cyclobutene (ca. 0.05 M) and cyclohexane (0.001 M). Aliquots (ca. 3 mL) were placed in 1-cm Suprasil cuvettes containing a small magnetic stirrer, sealed with rubber septa, and deoxygenated with a stream of dry argon. Photolyses were carried out using a Lambda Physik Compex 120 excimer laser (193 nm; \sim 25-ns, \sim 30-mJ pulses delivered with a repetition rate of 0.5-Hz), a 16-W Philips 93106E zinc resonance lamp, or a 16-W Philips 93107E cadmium resonance lamp. Solutions were stirred vigorously throughout the photolyses. Aliquots were removed from the cells by microliter syringe at suitable photolysis intervals and analyzed by GC. Product formation was monitored as a function of photolysis time in all cases. The data in Table 1 were determined by triplicate analyses of GC traces at the maximum conversion investigated, whereas those in Table 2 were determined from the slopes of plots of the product peak areas relative to that of the internal standard versus % conversion, after correction of the data with the FID response factors (determined from working curves). They were also corrected for secondary diene photoisomerization, as discussed in the Results section. Conversion scales for these plots were determined from the GC traces at maximum conversion.

The photolysis of **1** (0.41 g, 5.0 mmol) in methanol (50 mL) was carried out with the 228-nm light source in a Suprasil quartz immersion well apparatus equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet. Monitoring of the photolyzate at low conversions by capillary GC revealed the formation of **3**, **5**, and three new products, which eluted with longer retention times and were just well-enough resolved to determine that they were formed in equal yields. Irradiation was continued to \sim 80% conversion of **1** (14 days), with no change in the relative yields of the five photoproducts. The mixture was extracted with pentane (4 \times 25 mL), and the pentane extracts were then concentrated by distillation to a volume of ca. 1.0 mL. Semipreparative gas chromatography (UCW-982) allowed fractionation of the three major components of the mixture, which each consisted of one major component (70–80%) contaminated with small amounts of one or both of the others. The major components of each fraction were identified as **7–9** (in the order of their elution from the GC column) on the basis of the following ¹H NMR and GC/MS evidence. **3-Methoxy-2,3-dimethylcyclobutene (7)**: ¹H NMR δ 1.33 (s, 3H), 1.59 (s, 3H), 2.15–2.59 (m, 2H), 3.23 (s, 3H), 5.79 (s, 1H); MS *m/e* (I) 112 (27), 111 (12), 97 (100), 86 (33), 79 (37), 72 (68), 67 (30), 59 (21), 53 (28), 43 (84), 41 (52), 39 (42), 29 (21). **1-Methoxy-1-methyl-2-methylenecyclobutane (8)**: ¹H NMR δ 1.35 (s, 3H), 2.39–2.15 (m, 4H), 3.24 (s, 3H), 4.86–4.94 (dt, 2H); MS *m/e* (I) 5, 111 (11), 97 (79), 86 (21), 72 (100), 53 (19), 43 (69), 42 (41), 41 (26), 39 (39). **1-Methoxy-1,2-dimethylcyclobutane (9)**: ¹H NMR δ 0.93 (d, 3H), 1.15 (s, 3H), 1.56–2.00 (m, 5H), 3.14 (s, 3H); MS *m/e* (I) 97 (3), 86 (87), 72 (100), 71 (42), 55 (22), 43 (44), 42 (37), 41 (25), 39 (23).

Photostationary-state compositions for **6** at 228 nm were determined by photolyzing separate samples of *EE*- and *EZ*-**6** (7 μ L in 1 atm of SF₆ for gas-phase experiments or deoxygenated 0.05 M solutions in hexane), with periodic monitoring by GC, until common diene distributions were obtained.

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