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Photodissociation at 193 nm of Cyclooctatetraene and Styrene into Benzene and Acetylene

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When irradiated in a molecular beam at 193 nm, both cyclooctatetraene and styrene dissociate into benzene and acetylene. The average kinetic energy release is 12% of the available energy in both cases. So that the mechanism of the dissociation of styrene could be determined the ratio of mass 26 to mass 27 (C_2H_2/C_2HD) was measured for $C_6H_5CDCH_2$ and $C_6D_5CHCH_2$ and found to be 1.46 ± 0.10 and 2.29 ± 0.10, respectively. These numbers rule out cyclooctatetraene as an intermediate in the dissociation of styrene. A bicyclo[4.2.0]octa-2,4,7-triene intermediate which can tautomerize by 1,3 hydrogen atom jumps in the smaller ring explains all the experimental results.

Introduction

The rearrangements and dissociations of complex organic molecules under the action of light are rich fields in photochemistry. These reactions can be roughly described in mechanistic terms but it is a challenge to exploit physical techniques in order to understand the mechanism more precisely. Ultrafast spectroscopy permits, in principle, direct observation of the process but, in practice, the probing photon may have too low an energy to be absorbed by the system. Also, many transformations being completed on a subpicosecond time scale are difficult to observe during their course. Less demanding is the observation in the gas phase of the (nonequilibrium) final state distribution of the fragments after the dissociation is complete but before collisions have occurred.

In the present work we study the breakup of an eight-membered carbon atom ring, cyclooctatetraene, C_8H_8, into the more stable six-membered ring, benzene, and acetylene. We have previously shown that while benzene is very stable with respect to breakup into three acetylenes, substitution of CH groups by nitrogen atoms destablizes the ring so that *s*-triazine can be dissociated into three hydrogen cyanide molecules.[1,2]

Cyclooctatetraene (COT) has a complex photochemistry which is hinted at by the energy diagram of Figure 1. Depending on conditions such as photon energy and the presence or absence of solvent molecules, COT has been observed to photodissociate into benzene and acetylene and also to isomerize. The isomers include bicyclo[4.2.0]octa-2,4,7-triene (BOT), tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (semibulvalene, SBV), 1,5-dihydropentalene (DHP), and styrene (in minor amounts).[3] BOT has been isolated only at low temperatures in a matrix.[4] It is 6.5 kcal/mol higher in energy than COT and quickly isomerizes to COT at room temperature. The experiments reported here measured the kinetic energy distribution of the acetylene and benzene molecules dissociated at 193 nm from cyclooctatetraene and three different isotopic variants of styrene. The overall conclusion is that BOT stands, so to speak, at the doorway of the dissociation exit channel.

Experimental Section

A detailed description of the photofragment spectrometer has been presented elsewhere.[5] A new piezoelectric pulse molecular beam valve (Lasertechnics, LPV) with a 1-mm nozzle was used in this experiment. Due to the low vapor pressure of the samples, helium was bubbled through at 5 psig to increase the sample throughput. The molecular beam, entering into the reaction chamber through a skimmer, was crossed with an ArF excimer laser (193 nm) at a right angle. Orthogonal to the beam and laser was the quadrupole mass spectrometer with electron bombardment ionizer to ionize and mass analyze the photofragments collected through the detector aperture in front of the ionizer. The ion pulses registered in the channeltron multiplier from the transmitted photofragments were sent to a LeCroy 3500 multichannel analyzer system (resolution: 1 μs) for data averaging and storage.

Cyclooctatetraene and styrene (Aldrich) had a purity of 98%. Styrene-α-d_1, and styrene-*2,3,4,5,6*-d_5 from Merck isotopes were found by NMR to have isotopic purity better than 98%.

Results

Mass Analysis of the Photofragments. Examination of the photofragmentation pattern can directly shed light on the possible course of dissociation. Photodissociation of cyclooctatetraene at 193 nm generated C_2H_2 (mass 26) as the only light photofragment which agrees with an early study.[6] Photodissociation of sytrene at 193 nm also produced C_2H_2 as the only light photofragment. C_6H_6 (mass 78) is thus the only heavy photofragment (and a factor of three slower because of conservation of momentum) in both processes although it was not resolved from the background noise in the time-of-flight spectra within a reasonable amount of data acquisition time. The orthogonal orientation of the mass detector to the molecular beam dictates a preferential detection of the faster (light) fragments as compared to the slow (heavy) ones. Both mass 26 (C_2H_2) and mass 27 (C_2HD) appeared to be the photofragments of the two different deuterium-substituted styrenes and will be discussed later.

Translational Energy Distributions. The translational energy distribution (TED) of the photofragment can be unequivocally obtained from its time-of-flight (TOF) distribution. C_2H_2 TOF distributions from photolysis of cyclooctatetraene and styrene are shown in Figure 2. Both were taken with ArF laser pulses at 2 Hz for 1 h. Each pulse was about 20 ns in time and 200 mJ in energy. Apparently the signal intensity is peaked at a shorter flight time for cyclooctatetraene than for styrene which can be attributed to the higher heat of formation of cyclooctatetraene as compared to styrene.

The translational energy of a photofragment in the parent-molecule frame is related to the apparent arrival time t

$$E_T = \tfrac{1}{2}m[l^2/(t - t_d)^2 + c^2] \qquad (1)$$

where l is the flight path to the ionizer, t_d is the ion drift time which can be calibrated from the drift times of the various background masses, and c is the rms velocity of the beam. Because large nozzle size and low stagnation pressure were used, beam velocity was very close to the rms velocity of an effusive beam which was confirmed by the optimum delay time of the laser triggering with respect to the beam valve opening. The TOF

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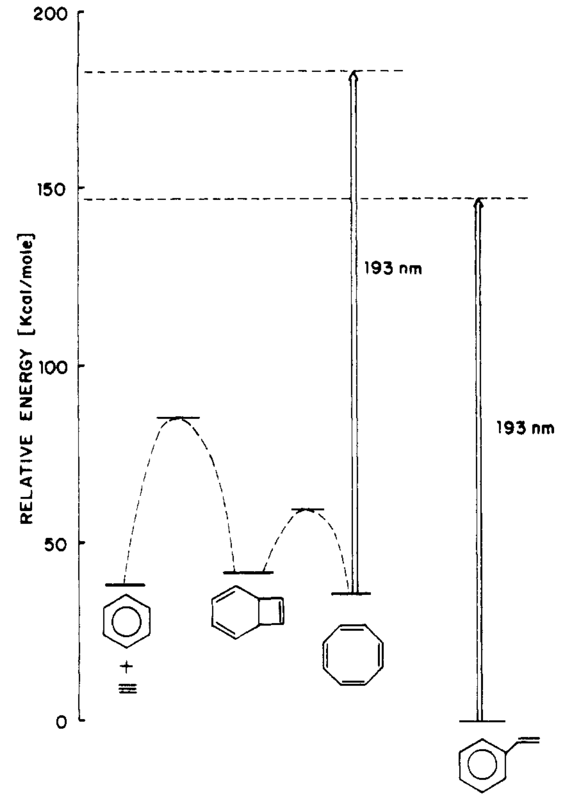

Figure 1. Energy levels of C_8H_8 systems.

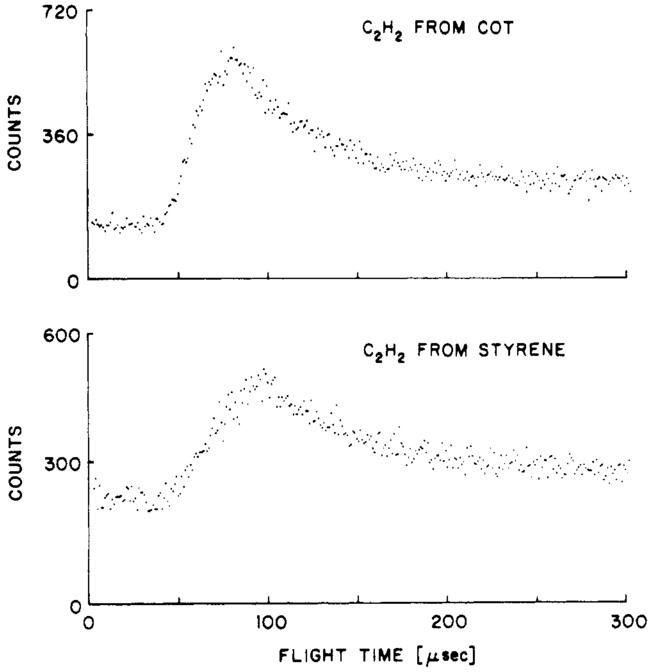

Figure 2. Time-of-flight distributions of acetylene fragments from the photolysis of cyclooctatetraene and styrene at 193 nm.

distribution measured in the lab frame can be converted to the TED by a suitable transformation.

The TED's of the C_2H_2 from both species are shown in Figure 3, where average translational energies are also designated.

Isotopic Branching Ratios of D-Substituted Styrenes. Following the detection of both mass 26 and mass 27 photofragments from D-substituted styrenes, the branching ratios of the two isotopic products were determined from the respective TOF distributions. The main peak (from 50 to 200 μs) was integrated above the background level which was the average count of the channels preceding the peak. The number of counts in each channel was divided by the corresponding time of flight in order to correct for the fact that slower fragments have a greater probability of being detected. A total of four hours of data accumulation for each was used to extract the ratios. The results (mass 26:mass 27) are 1.46 ± 0.10 for styrene-α-d_1 ($C_6H_5CD{=}CH_2$) and 2.29 ± 0.10 for styrene-*2,3,4,5,6*-d_5 ($C_6D_5CH{=}CH_2$) and will be discussed later. Figure 4 shows a comparison of the TOF distribution of mass 26 with that of mass 27 for $C_6D_5CH{=}CH_2$.

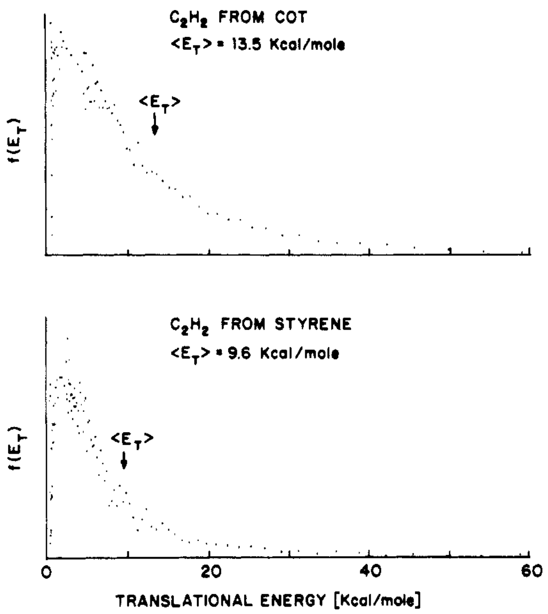

Figure 3. Translational energy distributions of acetylene fragments from the photolysis of cyclooctatetraene and styrene at 193 nm.

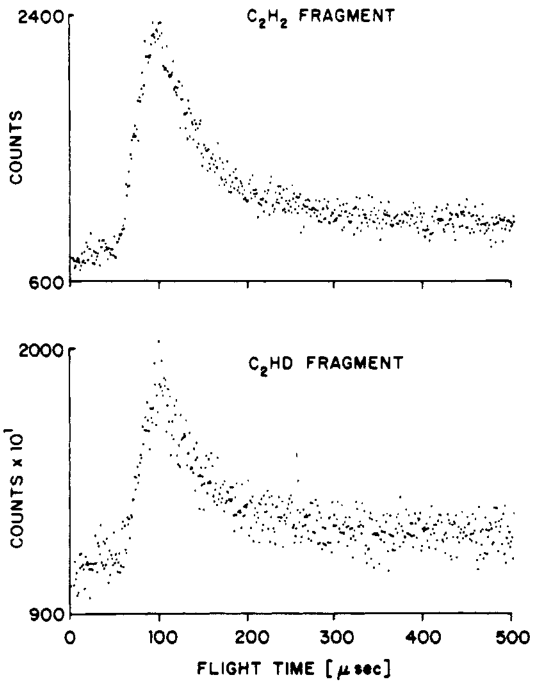

Figure 4. Time-of-flight distributions of mass 26 (above) and mass 27 (below) fragments from $C_6D_5CHCH_2$, each having 4 h of data accumulation.

TABLE I[a]

	E_{aval}	$\langle E_T(C_2H_2)\rangle$	$\langle E_T\rangle$	$\langle E_T\rangle/E_{\text{aval}}$
cyclooctatetraene	144.8	13.5	18.0	0.124
styrene	109.0	9.6	12.8	0.117

[a] $\langle E_T(C_2H_2)\rangle$ is the average kinetic energy of the acetylene fragment. $\langle E_T\rangle$ is the average total kinetic energy of both fragments. All energies are in kcal/mol.

Discussion

Styrene, COT, and BOT. Results for the average fraction of available energy released as translational energy, $\langle f_T \rangle$ are summarized in Table I. The fact that both COT and styrene although of grossly different structure yield the same benzene–acetylene pair on optical excitation is a hint that they may dissociate throught the same intermediate. The additional fact that $\langle f_T \rangle$ is the same in both cases, i.e., 12%, also points in the same direction.

Each of the molecular species COT, BOT, styrene, and the benzene–acetylene pair represents a particular minimum on the same electronically nondegenerate potential surface. This means that, when electronically excited, COT, BOT, and styrene must move on an excited surface which correlates to a benzene–acetylene pair in which one of the molecules is electronically excited. The potential minima of the lowest excited states of benzene and acetyene are at 38 086 (108.9 kcal/mol) and 42 198 $\mathrm{cm^{-1}}$ (120.6 kcal/mole) above the potential minima of their respective ground states. The available energy (Table I) is sufficient to excite one of these molecules. Nevertheless, no UV or visible emission was observed when COT and styrene were exposed to 193-nm light. It is thus established that internal conversion to the electronic ground state must take place. Does it take place immediately after excitation or just prior to the final step of separation of the fragment? This question cannot be answered completely rigorously but arguments will be given tending to show that internal conversion in BOT immediately precedes dissociation.

The mechanisms may be written symbolically as follows

$$\mathrm{COT} \xrightarrow{h\nu} \mathrm{COT}^* \rightarrow \mathrm{BOT}^* \rightarrow \mathrm{BOT}^\dagger \rightarrow \mathrm{C_6H_6} + \mathrm{C_2H_2} \quad (\mathrm{I})$$

$$\mathrm{styrene} \xrightarrow{h\nu} \mathrm{styrene}^* \rightarrow \mathrm{BOT}^* \rightarrow \mathrm{BOT}^\dagger \rightarrow \mathrm{C_6H_6} + \mathrm{C_2H_2} \quad (\mathrm{II})$$

An initial argument that internal conversion takes place later rather than earlier in the overall process is based on the kinetic energy distributions. If we assume that every final state (with the same energy) in a dissociation is equally likely to be occupied then we find that the relative translational energy distribution is given by

$$f(E_T) = N(E - E_T)^n E_T^{1/2} \qquad (2)$$

where N is a constant, E is the available energy, and n is the number of harmonic oscillators in the system. From this distribution one finds that the average fraction of energy released as translational energy is

$$\langle f_T \rangle = \langle E_T \rangle / E = 3/(2n + 5) \qquad (3)$$

If $\langle f_T \rangle = 0.12$ as with COT and styrene, then $n = 10$. In fact there are 37 vibrational modes in a benzene–acetylene pair.

Two explanations can be given for this discrepancy. One is that incomplete vibrational relaxation has taken place which is characteristic of a very fast decomposition. An alternate explanation is that vibrational equilibrium prevails at the transition state, i.e., at the specific region of configuration space in which product molecules are formed. On entering the product side of the transition state, the potential energy is released as translational energy. If there is a barrier of height V in the exit channel, statistical equilibrium prevails and no translational energy is lost to vibration as the fragments separate, the distribution of translational energy will be given by a function similar to eq 2:

$$f(E_T;V) = N(E - V - (E_T - V))^n (E_T - V)^{1/2} \qquad (4)$$

$$\langle f_T \rangle = {}_T\langle E_T \rangle / E = V/E + (3/(2n + 5))(E - V)/E \qquad (5)$$

If $\langle f_T \rangle = 0.12$, then $V/E = 0.080$. This means that cyclooctatetraene and styrene would have 12 and 9 kcal/mol barriers, respectively. We prefer the first explanation because (a) a common intermediate would have a common potential barrier and (b) extensive hydrogen shifts occur in the excited state (see below) so that the rate of dissociation would appear to be mainly limited by the rate of internal conversion.

Mechanistic Study with Deuterium-Substituted Styrenes. The experiments so far discussed have suggested that COT and styrene dissociate through the same intermediate but have not provided direct evidence that this intermediate is BOT. Two deuterated styrenes were investigated to see whether styrene passes through an eight-membered ring COT structure before dissociating. The compounds chosen, $\mathrm{C_6H_5CDCH_2}$ and $\mathrm{C_6D_5CHCH_2}$, would then yield a $\mathrm{C_2H_2/C_2DH}$ ratio (i.e., mass 26/mass 27) of 3 and 0.3, respectively. The experimental values of the ratios were 1.46 ± 0.10 and 2.29 ± 0.10, respectively. This negative result is in accord with the fact that when photolyzed COT either dissociates to benzene and acetylene or isomerizes to a variety of products including styrene but styrene does not isomerize to COT.

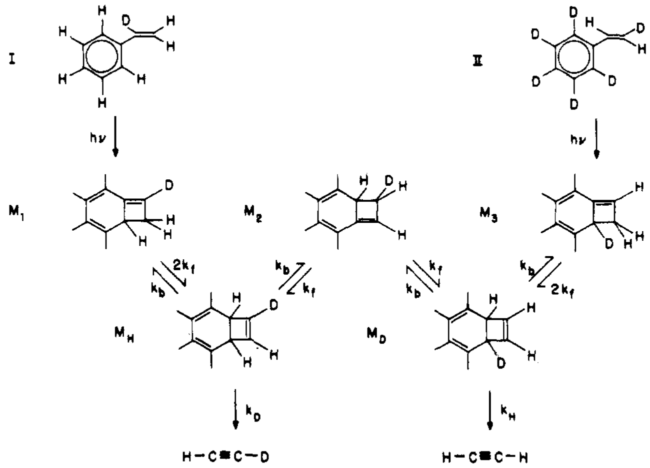

Figure 5. Mechanistic steps assumed in the photodissociation of deuterium-labeled styrene. Open-ended bonds around 6-membered rings stand for –H if starting with compound I, for –D if starting with compound II.

Having now accepted that the carbon atoms of the acetyene product are those of the original vinyl group, our first question was which hydrogen atom is transfered to the benzene ring, the α or one of the two β hydrogen atoms. The use of $\mathrm{C_6H_5CDCH_2}$ which resulted in the mass 26/27 ratio of 1.46 seemed to imply that either the α or the β hydrogen atom could jump. The compound $\mathrm{C_6D_5CHCH_2}$ yielded a ratio of 2.29; from this result it became clear that hydrogen atoms not only jump from the side chain to the ring but also from the ring to the side chain. The case for a BOT intermediate in which hydrogen atoms could rapidly interchange had become compelling.

Let us now consider ring closure to form the BOT intermediate. A series of intermediates is shown in Figure 5. The compounds $\mathrm{M_D}$ and $\mathrm{M_H}$ are isotopically labeled BOT molecules which can dissociate into heavy (DCCH) and light (HCCH) acetylene, respectively. The tautomers $\mathrm{M_1}$, $\mathrm{M_2}$, and $\mathrm{M_3}$ are assumed to be unable to decompose directly. If the rate of interchange of the five species were very rapid compared to their rates of dissociation the mass 26/27 ratio would be exactly the same for the two compounds. As the ratios are rather different the rate of dissociation cannot be slow compared to the rate of hydrogen atom jumps. On the other hand, the rate of dissociation is not fast compared to the rate of hydrogen atom jumps. If they were, then $\mathrm{C_6H_5CDCH_2}$ would yield only heavy acetylene and $\mathrm{C_6D_5CHCH_2}$ would yield only light acetylene. Thus we conclude that the rate of dissociation of the BOT into benzene and acetylene is comparable to its rate of tautomerism. In fact we have integrated the seven rate equations implied by Figure 5 and obtained good agreement with experiment using the parameters $k_b/k_f = 2.2$, $k_H/k_f = 0.40$, and $k_D/k_f = 0.20$. Nothing is claimed for these parameters except that they are not unreasonable and using them leads to the prediction that $\mathrm{C_6H_5CDCH_2}$ would yield a ratio of 1.8 for mass 26/mass 27.

Even when starting with $\mathrm{C_6H_5CDCH_2}$ (compound I in Figure 5) we obtain an excess of light over heavy acetylene which implies that the rate of dissociation of BOT in the form of $\mathrm{M_D}$ is slower than that of $\mathrm{M_H}$. A plausible reason is the Franck–Condon factors associated with the bent acetylene as it dissociates. These factors will be smaller for HCCD which for the same configurational energy will be excited into states of higher vibrational quantum numbers than HCCH.

As complex as it appears, Figure 5 is a simplified diagram. The compounds M_D, M_2, and M_H all could occur as cis and trans forms which may have different probabilities of dissociation. To investigate these questions one would have to study the dissociation of *cis-* and *trans-*C_6H_5CHCHD. For the time being in the interests of simplicity the cis and trans isomers have been lumped together as single species.

Relation to Previous Photochemical Studies. Previous photochemical studies on cyclooctatetraene have been reviewed by Dudek et al.[3] The quantum yield for dissociation is 0.2 at 302 nm and increases with increasing photon energy. The present experiment is a little difficult to compare with previous ones. All reported studies were in the region of the first (forbidden) $^1A_2 \leftarrow {}^1A_1$ absorption band whereas the present studies are near the peak of the strongly allowed $^1E \leftarrow {}^1A_1$ transition at 193 nm. Previous work involved product analysis after several minutes or more of irradiation. The molecular beam experiment measures only dissociation products. Nevertheless, we believe that at these high energies dissociation is the major or perhaps the only process. The average internal energy (see Table I) of the photolyzed COT molecule is 127 kcal/mol which is sufficient we think to overcome all barriers to dissociation which thermodynamically requires only 3 kcal/mol. Dudek et al.[3] concluded that internal conversion to a hot ground state precedes isomerization or dissociation of COT.

A correlation theorem assures us that internal conversion must precede dissociation. The ground states of cyclooctatetraene, styrene, and the acetylene–benzene pair correspond to different minima on the same singlet nondegenerate potential surface. Electronic excitation of COT or styrene is to a surface which necessarily dissociates to an excited state of benzene, of acetylene, or both. Because only ground state products are observed, internal conversion must precede dissociation.

No dissociation process has been reported for styrene but this may well be because the wavelengths used were ≥250 nm. The 1,3 migrations of the hydrogen atoms demonstrated here are suprafacial migrations because of steric constraints in the four-membered ring. However suprafacial 1,3 migrations can only take place in an excited electronic state.[7] Thus we conclude that the sequence of events following electronic excitation of styrene is hydrogen atom shifts, internal conversion to the ground state, and fragment separation.

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Registry No. Cyclooctatetraene, 629-20-9; styrene, 100-42-5.

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