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Unimolecular dissociation of cyclopentadiene and indene

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The dissociation of hydrogen atoms from the methylene group of cyclopentadiene (CP) and indene (ID) excited with a 193 nm photon has been studied by hydrogen atom laser induced fluorescence. The rate of dissociation of IND was 7.4×10^6 s⁻¹ but that of CP was too fast to measure. The ratio of H atoms to D atoms generated from 5-deuteriocyclopentadiene (5-dCP) was 3.91 ± 0.46 . Rice-Ramsberger-Kassel-Marcus theory was used to calculate the rates of dissociation of CP and 5-dCP. The quantum yield for dissociating H atoms from CP was 0.85 ± 0.07 . The ejected H atoms have a Maxwell velocity distribution with temperatures which are equal to the vibrational temperatures, 3690 and 2479 K for CP and IND, respectively. The most important result of the work is this confirmation of an earlier finding on a different set of molecules that the translational temperature of the fragments *after* the dissociation is equal to the vibrational temperature *before* the dissociation. This is explained by the assumption that the motion of the fast, light hydrogen atom is partly decoupled from that of the heavier, slower atoms.

UNIMOLECULAR DISSOCIATION OF CYCLOPENTADIENE AND IDENE

The central aim of the theory of unimolecular reactions is to calculate the rate k(E) at which a molecule activated with an energy E will undergo a chemical change such as dissociation or isomerization remaining always on the same ground state potential surface. To test the theory one needs to prepare molecules with a known energy E and then measure the rate at which the molecule breaks apart. In addition to the rate measurement, one can, in principle, measure the distribution over the translational and internal states of the dissociation products.

The general case in which a molecule dissociates into two fragments which are themselves molecules is formidable because of the very large array of accessible internal states. Dissociation processes in which one of the products is an Sstate atom are simpler in that one of the fragments aside from spin, has at normal energies only one populated internal state. If the S atom is a light atom such as a hydrogen atom, there is a further advantage in that the translational energy distribution can be extracted from the Doppler broadened absorption spectrum.

To prepare electronic ground-state molecules with a known amount of internal energy it is convenient to use optical absorption provided that subsequent crossover to the ground state and internal vibrational redistributions are much faster than the rate k(E). The molecule chosen must be of an intermediate size. If it is too small, either dissociation will take place on an excited state potential surface or dissociation times will be in the difficultly measured subpicosecond range. If the molecule is too large, it will decompose so slowly that collisions will occur before dissociation thus altering the energy and destroying the condition of a collisionless process.

In previous studies^{1,2} we have measured the rate of dissociation and average translational energy of a set of energized methylated benzenes and pyrazines. The rate constants were derived from a measurement of the laser induced fluorescence intensity as a function of time and the average translational energy from the second moment of the Gaussian shaped excitation spectrum. As the number of atoms in the molecule increased the rate of dissociation and the average translational energy decreased. The velocity distribution of the H atoms was Maxwellian with a temperature which was the same as the vibrational temperature *before* dissociation.

The transition state for any unimolecular dissociation, the region in configuration space which marks the boundary between molecule and fragments is difficult to observe experimentally. For a methyl group attached to an aromatic, e.g., toluene there is fairly complicated distortion required to form a complex of a benzyl radical and a H atom, assuming that the transition state resembles the products. We have therefore sought a model system in which the deformation of the original molecule to form the transition state is simpler. For cyclopentadiene (CP) and its relative, indene (IND) (Fig. 1), the transition state might only involve a rotation of the CH₂ group with perhaps a change in the HCH angle.

We have not found any published reports on the gas phase photochemistry of CP or IND except for the numerous observations, e.g.,^{3,4} that irradiation at 248 nm of CP produces cyclopentadienyl radical. Using 193 nm light, in the gas phase CP and IND are readily dissociated

cyclopentadiene $(C_5H_6) + hv$

$$\rightarrow$$
 cyclopentadienyl + H, (1)

indene(
$$C_9H_8$$
) + $h\nu \rightarrow$ indenyl + H. (2)

EXPERIMENT

The details of the experiment have been described previously.⁵ In brief, excimer laser light excites a gas under the pressure of 20 mTorr in a cell and after a short delay laser generated 121.6 nm light excites H atom to the 2p state and the resulting fluorescence is detected in the direction perpendicular to the plane of the two laser beams. A series of quartz Yi, Chattopadhyay, and Bersohn: Dissociation of cyclopentadiene and indene



FIG. 1. (a) Cyclopentadiene. (b) Indene.

plates was used to attenuate the 193 nm laser beam in order to vary the intensity.

Cyclopentadiene monomer was produced by distilling its dimer (Aldrich 95%) and indene (Aldrich 98%) was used as received. 5-deuteriocyclopentadiene, C_5H_5D was made by fractional distillation of cyclopentadienylthallium, C_5H_5T1 (Aldrich 96%) and D_2SO_4 (Aldrich 99.5%) in $D_2O.^{\circ}$

RESULTS

Hydrogen atom signal vs photolysis laser fluence

It is not unusual that two photon processes are involved and even dominant in the laser photodissociation of a molecule. The atomic H laser induced fluorescence (LIF) signal is plotted vs the photolysis laser fluence in Fig. 2. Starting at around 30 mJ/cm² the H atom yield ceases to be linear and shows a quadratic dependence on the laser intensity. As our intention is to prepare molecules with a known energy *E*, multiphoton processes must be avoided. Therefore all experiments were performed with <25 mJ/cm² of ArF laser fluence.

H atom quantum yield from cyclopentadiene

The absolute quantum yield, $\phi_{\rm H}$, for the process $C_5H_6 \rightarrow C_5H_5 + H$ was obtained by comparison with the quantum yield for the production of H atoms from H_2S which was assumed to be one. The ratio of the LIF signal of



FIG. 2. Hydrogen atom signal vs photolysis laser fluence.

H from $C_{s}H_{6}$ to that from $H_{2}S$ was measured. The following equation was then used to calculate $\phi_{H}(C_{5}H_{6})$:

$$\frac{A_{\rm H}({\rm C}_{\rm 5}{\rm H}_{\rm 6})}{A_{\rm H}({\rm H}_{\rm 2}{\rm S})} = \frac{\epsilon_{{\rm C}_{\rm 5}{\rm H}_{\rm 6}}P_{{\rm C}_{\rm 5}{\rm H}_{\rm 6}}\phi_{\rm H}({\rm C}_{\rm 5}{\rm H}_{\rm 6})}{\epsilon_{{\rm H}_{\rm 5}{\rm S}}\rho_{{\rm H}_{\rm 5}{\rm S}}\phi_{\rm H}({\rm H}_{\rm 2}{\rm S})},$$
(3)

where ϵ_i and A_i are the molar extinction coefficient and the area under the fluorescence excitation curve of species *i*. The final result is a quantum yield $\phi_{\rm H} = 0.85 \pm 0.07$. This result shows that the process $C_5H_6 \rightarrow C_5H_5 + H$ is the dominant channel.

Dissociation rate constants and average translational energies

Figure 3(a) shows the time dependence of the H atom signal from CP irradiated at 193 nm. The decay of the signal is mainly due to a net motion out of the region of observation. The formation rate of H atoms from CP is too fast to be measured by our experimental apparatus. The minimum delay time between our pump and probe lasers is about 100 ns. Thus we estimate that the dissociation rate constant $> 10^7 \text{ s}^{-1}$. As can be seen in Fig. 3(b), the fluorescence intensity of the H atom generated from indene shows a small increase as the delay time is changed from 150 to 250 ns. Using a growth curve of the form $I(t) = N [\exp(-k_1 t)]$ $-\exp(-kt)$] where N is a normalizing constant, k is the rate constant for formation of H atoms, and k_1 is the rate of decay of the atomic concentration in the region of observation due to a net outward motion, k was found to be $(7.4 \pm 1.0) \times 10^{6} \, \mathrm{s}^{-1}$.

The full widths at half maximum (FWHM) of the Gaussian shaped Doppler profiles of the nascent H atoms produced from the photodissociation of CP and IND were 3.75 ± 0.26 and 2.94 ± 0.18 cm⁻¹, respectively. These values correspond to average relative kinetic energies of 12.2 ± 1.8 and 7.5 ± 0.9 Kcal/mol.

H/D ratio of C₅H₅D

The branching ratio for the production of H and D atoms from the photodissociation at 193 nm of 5-deuteriocyclopentadiene was measured by comparing the areas under the LIF excitation spectra of H and D atoms. The H/D ratio has an average value 3.91 ± 0.46 which is higher than that found in deuterated toluene and ethylene.^{1,7} There were no significant changes in the H/D ratio even when the intensity of the photolysis laser was varied from 6 to 30 mJ/cm².

DISCUSSION

Bond dissociation energy

The C-H bond energy of CP can be determined from the heats of formation of cyclopentadiene⁸ (room T), cyclopentadienyl⁹ (room T), and H(0 K) which are respectively 31.94 ± 0.28 , 58 ± 2 , and 51.63 Kcal/mol. The resulting bond energy is 78 ± 2 Kcal/mol. The C-H bond energy of the CH₂ group in IND has been reported to be 84 ± 3 Kcal/mol.¹⁰ It is difficult to justify this larger value on theoretical grounds. The simplest version of Huckel molecular orbital theory in which all energies are expressed in terms of a common resonance integral β yields for the π electron energies of

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FIG. 3. Growth and decay curve of fluorescence intensities of H atoms from (a) cyclopentadiene and (b) indene.

butadiene, CP, styrene, and IND the values 4.473β , 5.854β , 10.424β , and 11.875β . These numbers lead to the conclusion that the C-H bond in IND is weaker by $0.069\beta = 1.4$ Kcal/mol if β is taken to be 20 Kcal/mol. On the other hand effects from the different remote atoms may be of the order of 1–2 Kcal/mol. Our compromise is to assume that the C-H bond energies in both CP and IND are the same.

The vibrational and translational temperatures

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After CP or IND absorbs a relatively high energy photon rapid internal conversion occurs to a hot ground state. This process is interesting in itself but happens orders of magnitude faster than the time scale for dissociation. The hot molecule is assumed to have an internal vibrational temperature defined by Eq. (4),

$$E + \sum_{i} h\omega_{i} / [\exp(h\omega_{i}/kT) - 1]$$

= $\sum_{i} h\omega_{i} / [\exp(h\omega_{i}/kT_{V}) - 1].$ (4)

Here *E* is the photon energy at 193 nm (147.8 Kcal/mol), *T* is the room temperature, and ω_i are the vibrational frequencies of the CP or IND molecule. The calculated T_V for CP and IND are 3690 K and 2479 K, respectively. Table I lists all the relevant energies.

As shown in Fig. 4 the Doppler profile of the nascent H atoms from the photodissociation of CP and IND are Gaussian which in turn implies that the velocity distribution of the H atoms is Maxwellian. The translational temperature, T_T of the H atoms can be calculated from the formula

 $T_T = (m/8kln2) (c\delta v/v_0)^2$ where δv is the FWHM. The calculated translational temperatures are 4084 \pm 585 K for CP and 2510 \pm 298 K for IND which are, within the error limits, the same as the vibrational temperatures, T_v (see Table I). The same equality was found in the methylated benzenes.^{1,2} It is not perfectly clear why this should be true. The vibrational temperature is a property of the molecule *before* dissociation. The translational temperature is a property of the fragments *after* the dissociation.

Here is an explanation for the equality of the two temperatures. The hydrogen atom is so much lighter than the other atoms that its states can be calculated as if the other atoms were frozen. The motion of the heavier atoms will be so slow that the hydrogen atom will remain adiabatically in the same state. However the life time of the energized molecule is so long that the hydrogen atom will come to thermal equilibrium with the other atoms by occasional nonadiabatic transitions. The hydrogen atom passes through the transition state very quickly so that its motion is decoupled from that of the other atoms. Thus the large amount of energy required for the dissociation is extracted from the other modes. At the transition state the reaction coordinate contains thermal energy at temperature T_V plus the dissociation energy. It could be argued that there is a barrier to the recombination of the H atom and the corresponding radical. However any barrier in the exit channel and subsequent dynamics should be virtually identical for CP and IND. Nevertheless the translational energy releases are quite different. We therefore think that the barriers if they exist are low and

TABLE I. Average vibrational temperatures of cyclopentadiene and indene after absorbing a 193.3 nm photon; average relative translation energies of the fragments. $E_{AVAL} = E(\text{photon}) - \text{bond energy}, [f_T] = \langle E_T \rangle / E_{AVAL}$.

	EAVAL	FWHM	$\langle E_T \rangle$	$\overline{T_{T}}$	T_{ν}	
Compound	(Kcal/mol)	(cm ⁻¹)	(Kcal/mol)	(K)	(K)	$[f_r]$
CP Indene	70 70	3.75 ± 0.26 2.94 ± 0.18	12.2 ± 1.6 7.5 ± 0.9	4084 ± 585 2510 ± 298	3690 2479	$\begin{array}{c} 0.17 \pm 0.02 \\ 0.11 \pm 0.01 \end{array}$

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FIG. 4. Fluorescence excitation spectrum of H atom from (a) cyclopentadiene and (b) indene at 193.3 nm.

scarcely alter the H atom kinetic energy. The adiabatic motion hypothesis accounts straightforwardly for the temperature equality which now has been seen in too many different molecules to be a coincidence.

The available energy, E_{AVAL} in Table I is the photon energy minus the C-H bond energy. The average fraction $\langle f_T \rangle$ of the available energy released as a translational energy, $\langle f_T \rangle$ is 0.17 ± 0.02 and 0.11 ± 0.01 for CP and IND, respectively. Similar results were found for a homologous series of methylbenzenes whose $\langle f_T \rangle$ values decrease from 0.13 for toluene to 0.07 for tetramethylbenzene. Evidently as the number of modes increase the vibrational temperature and the energy released into translation both decrease.

The quantum yield for generating H atoms from CP was found to be 0.85 ± 0.07 . In solution CP is photochemically converted to a less stable two ring isomer,¹¹ but in the gas phase that isomer would also dissociate. Our speculation is that the other channel with yield 0.15 ± 0.07 is the formation of H₂ molecules and the carbene, cyclopentadienylidene. The latter is a known species which has been photochemically generated in another way.¹² This channel requires about 10 Kcal/mol more energy than the H atom channel and therefore is disfavored.

RRKM calculation of *k(E)*

RRKM theory is a statistical theory which calculates the rate at which a system crosses a hypothetical transition state with the assumption that all the degrees of freedom of the molecule are active, i.e., can contribute their nonfixed energy to the reaction. At the transition state the dissociation coordinate is normal to the dividing surface between reactant and product. Cyclopentadiene¹³ and cyclopentadienyl¹⁴ are planar. If we ignore the differences in C–C bond lengths, the dynamics of the transition state of CP can be described as follows: As the H atom departs from cyclopentadiene, the other H atom of the methylene group rotates toward the plane of the ring and the HCH bond angle distorts to around 90°. The threshold energy was taken to be 78 Kcal/mol, the same as the bond energy.

An activated 5-dCP decomposes in two major channels

$$C_5H_5D \rightarrow C_5H_5 + D, \tag{5}$$

$$C_5H_5D \rightarrow C_5H_4D + H.$$
(6)

The average H/D ratio, i.e., the ratio of the yields of these two channels is 3.91 ± 0.46 for 193 nm photons. The rate for each channel was calculated by RRKM theory. In the transition state only four of the 27 vibrational modes, the scissor, twist, wag, and rock of the CH₂ or CHD group are assumed to be different from those of the unactivated molecule. The frequencies used for the activated complexes of the two channels are listed in Table II.

In each activated complex the reaction coordinate was the C-D or C-H stretch. For the D elimination in (5) the CHD twist, wag, rock, and scissor were reduced from 1135 to 1000 cm^{-1} , from 1022 to 700 cm⁻¹, from 848 to 300 cm $^{-1}$, and from 1226 to 300 cm $^{-1}$, respectively. The transition state frequencies for the H elimination are affected to a larger extent than those for the D elimination. The reason is the mass difference between H and D which is assumed to reduce the four frequencies by a factor of $2^{1/2}$. Therefore the frequencies of the complex for the H elimination reaction (6) were taken to be 700, 490, 210, and 210 cm $^{-1}$, respectively. The RRKM result for the ratio of the rate constants, $k_{\rm H}/k_{\rm D}$ at 193 nm is 3.73 which agrees well with the experimental value of 3.91. The calculated rate constants, $k_{\rm H}(E)$ and $k_{\rm D}(E)$ are plotted in Fig. 5 vs photon energy for photodissociation in the range of 100-200 Kcal/mol.

To calculate the rate of H atom elimination from CP and IND the frequencies which differ in the transition state were assumed to be the same as in the transition state for the H atom elimination from 5-dCP. The full set of vibrational frequencies of indene have not been reported but were estimated from the known frequencies of the structurally similar and isoelectronic molecule indole.¹⁵ The results are $k(E) = 7.0 \times 10^9 \,\mathrm{s}^{-1}$ for CP and $6.2 \times 10^6 \,\mathrm{s}^{-1}$ for IND. The k(E) of IND from RRKM calculations is close to the ex-

TABLE II. Vibrational frequencies (cm⁻¹) assumed for the activated complex. All other frequencies are assumed to be the same in the activated complex as in the unactivated molecule.

Mode	(a) Ground state of 5-dCP	(b) D elimination	(c) H elimination	
		P R	B	
CH stretching	2889	2889	Reaction coord.	
CD stretching	2157	Reaction coord.	2157	
CHD scissor	1226	300	210	
CHD twist	1135	1000	700	
CHD wag	1022	700	490	
CHD rock	848	300	210	

perimental result deduced from Fig. 2 $(7.4 \pm 1.0) \times 10^6$ s⁻¹.

The numerical choices for the four frequencies assumed to be variable are, of course, rather arbitrary but are somewhat restricted by the necessity to fit the approximately 4/1H/D ratio. Once this fitting was done, however, the rate constant for dissociation of indene was calculated with no new assumptions; the real check of the theory is the semiquantitative fit of the theoretical and experimental values of this rate constant.

CONCLUSION

Two molecules, cyclopentadiene and indene each with a similar five membered ring containing a CH_2 group were activated with the same energy, 148 Kcal/mol. The small molecule, cyclopentadiene dissociated faster than the larger molecule, indene. In simple terms, it takes less time on the average for the necessary energy to accumulate in the weakest bond. Only a small fraction of the available energy ap-



FIG. 5. Rate constants vs photon energy for photodissociation of 5-dCP; (a) H atom elimination (b) D atom elimination.

pears as translational energy. However, the H atoms ejected from the larger molecule have lower kinetic energy. This rules out a substantial barrier in the exit channel which is essentially identical in the two molecules. Most important, and confirming the same result found in a set of methylated benzenes and pyrazines, the translational temperature of the H atom was found to be equal to the vibrational temperature of the hot parent molecule. In turn this implies that the H atom vibrational modes are in thermal equilibrium with the rest of the vibrational modes, but that on the way to the transition state, the H atom is decoupled and retains its initial thermal energy. The general equality, $T_T = T_V$, depends on this assumption of decoupling and therefore may be valid only for very light atoms such as hydrogen.

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