An element which clouds this interpretation is the possibility for preferential solvation of the apolar species by the larger, but also relatively less polar, cosolvent molecules considered. We have not invoked any need for preferential solvation by cosolvent in discussing the solvation mechanism, but it is reasonable to anticipate important quantitative contributions to the effectiveness of the cosolvent from this origin. For example, the data presented in the figure cited above also shows that urea is not unusually effective in solubilizing naphthalene. In fact, the smaller ethanol molecule is slightly more effective.

In conclusion, we believe that the present study, in combination with that presented in paper 1, is most consistent with the view that the critical feature of urea which leads to enhanced solubilization of apolar species is the simple displacement of a number of water molecules from the apolar solvation sphere. The significant influence of urea on the hydrogen bonding structure in the apolar region must, however, make an important quantitative contribution. In regard to the protein denaturing ability of urea, it is most reasonable to regard this as a result of the unusual *combination* of abilities including both the improved solvation of hydrophobic side chains and the ability to solvate polar groups, as suggested earlier.[13,16]

Acknowledgment. Support of the work reported here by grants from the National Institute of General Medical Sciences (GM 30452) and the Robert A. Welch Foundation is gratefully acknowledged. P.J.R. is an Alfred P. Sloan Foundation Fellow and the recipient of a Research Career Development Award (PHS No. CA00899) awarded by the National Cancer Institute, DHHS.

Registry No. Water, 7732-18-5; urea, 57-13-6.

Dissociation Dynamics of Photochemically Activated 3,5-Cycloheptadienone in the Gas Phase

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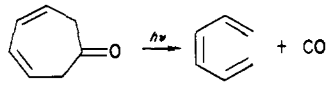
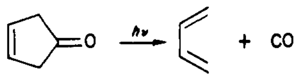
Abstract: Energy partitioning in the photoactivated fragmentation of 3,5-cycloheptadienone has been studied by using time resolved laser absorption spectroscopy. We have directly measured the CO product vibrational energy distribution and find that for excitation at 193 nm, N_0:N_1:N_2 = 1.00:0.33:0.09. Excitation at 249 nm yields N_0:N_1:N_2 = 1.00:0.24:0.04, and excitation at 308 nm yields N_0:N_1:N_2 = 1.00:0.14:0.02. The data at each excitation wavelength are consistent with a statistical model for energy disposal if the full reaction exoergicity is available to be randomly distributed among all the developing products' degrees of freedom. This suggests the products are strongly coupled well into the exit channel. These observations are contrasted with results on energy disposal for an apparently similar reaction, the dissociation of 3-cyclopentenone, where it was found that the full reaction exoergicity was not available to the products' vibrational modes. A mechanistically based model is suggested to account for the observed differences in energy disposal dynamics for these two ketones.

The exoergicity of a chemical reaction can be distributed in various ways among the products' vibrational, rotational, and translational degrees of freedom. The manner in which this energy is partitioned is determined by factors such as the transition-state geometry and the extent to which the internal and external degrees of freedom of the developing products are coupled with one another (i.e., exit channel effects). Measurements of energy distributions in the nascent products, prior to collisional relaxation, constitute a probe of reaction dynamics in the exit channel. In the case of thermally or chemically activated unimolecular dissociations, experiments typically yield a measure of the rate of conversion of activated reactant to transition state. This corresponds to information regarding the reaction dynamics on the bound side of the critical surface. Of course, this is precisely the problem encompassed by statistical unimolecular rate theories, such as RRKM theory.[1] In its conventional formulation, statistical rate theory cannot provide a model for dynamics in the exit channel. Although a variety of statistical[2,3] and nonstatistical[4] models for energy disposal have been proposed, none has proven to be of *general* use in predicting or rationalizing product energy distributions. The need for further experimental work along these lines is thus evident. This is particularly the case for larger polyatomic reactants where, until quite recently, little information has been available on energy disposal associated even with processes as "simple" as fragmentation reactions. In this article we discuss some results on energy partitioning in the photochemically activated dissociation of 3,5-cycloheptadienone (CHD), eq 1.



(1)

Our approach in this case is similar to that adopted in our studies of the dissociation dynamics of 3-cyclopentenone,[5,6] eq 2.



(2)

Specifically, nascent CO product vibrational energy distributions are determined by time-resolved laser absorption spectroscopy for several choices of photoactivation wavelength. The results are compared with distributions computed on the basis of a statistical model for energy partitioning. In this way, some insight can be obtained regarding the point in the exit channel where product internal energy distributions are established.

Reactions 1 and 2 can be characterized as cheletropic fragmentations.[7] This suggests that electronic or orbital symmetry conservation rules may provide a basis for predicting the facility

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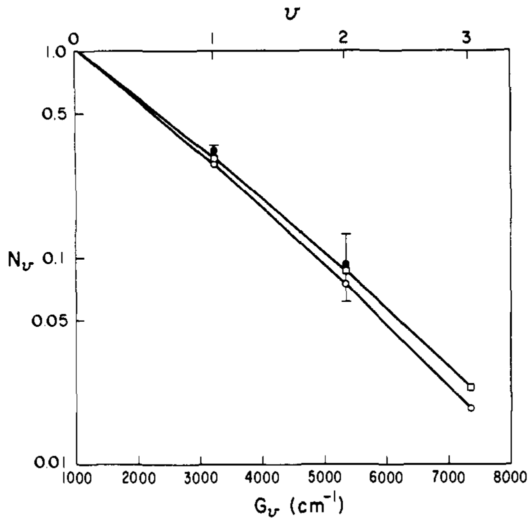

Figure 1. Vibrational energy distribution of the CO product formed by the photolysis of 3,5-cycloheptadienone at 193 nm: (●) experimental data; (□) distribution calculated by using eq 4 with an available energy E = 140 kcal/mol; (○) distribution calculated with an available energy E = 130 kcal/mol.

and mode (least motion vs. non-least motion) of these processes.[8] Of course, any such predictions are meaningful only if the reactions are concerted. We find significant differences in the extent of energy partitioning to products' internal degrees of freedom for reactions 1 and 2. This observation is discussed in terms of mechanistic models for the two processes, below.

Experimental Section

The instrumentation employed in our experiments has been previously described[5,6] and so will be outlined only briefly here. CHD at 0.05–0.5 torr is contained in an absorption cell of pathlength 13–100 cm. Photoactivation is accomplished with a rare gas halide excimer laser which provides ca. 15-ns pulses at 193, 249, or 308 nm depending on the fuel gases. Laser fluences of 1–5 mJ/cm^2 are typically employed. A continuous wave, tuneable CO laser is used to detect the CO photoproduct with vibrational state specificity. The CO laser is directed through the absorption cell, co-axially with respect to the excimer laser beam, and then onto an InSb detector. The detector output, which is a transient absorption curve for the CO laser line employed, is digitized and then signal averaged in a microcomputer. The overal detection system response time is $\lesssim$100 ns.

CHD was prepared according to literature methods.[9] In a separate set of experiments, CHD at ca. 0.5 torr was photolyzed with several thousand laser pulses at 193, 249, and 308 nm. In each case, products were collected and analyzed by conventional infrared and NMR spectroscopic methods.

Results

The photoexcitation of CHD in the gas phase at 193, 249, or 308 nm yields carbon monoxide and 1,3,5-hexatriene as the only observed products (see eq 1). The CO product of this fragmentation reaction is detected by CO laser absorption spectroscopy. Specifically, CO in state (v,J) resonantly absorbs the CO laser $P_{v+1,v}(J)$ line. Transient absorption curves are obtained by using laser lines corresponding to $v = 0$ to $v = v_m$. No absorption is observed for $v > v_m$. For all the experiments reported here, $v_m = 3$. This is determined by signal/noise, rather than thermochemical, limitations. In each case, absorption rise times are found to decrease with increasing pressure, with $p\tau_r \sim 2.5 \times 10^{-7}$ torr·s for all three UV excitation wavelengths. Absorption decay times are typically at least two orders of magnitude slower than the rise times, irrespective of the UV excitation wavelength. Under these conditions nascent CO product vibrational energy distributions can be determined from the (maximum) signal amplitudes of the transient laser absorption curves, as previously described.[5,6,10] The resulting distributions are shown in Figures 1–3 for photoexcitation wavelengths of 193, 249, and 308 nm, respectively.

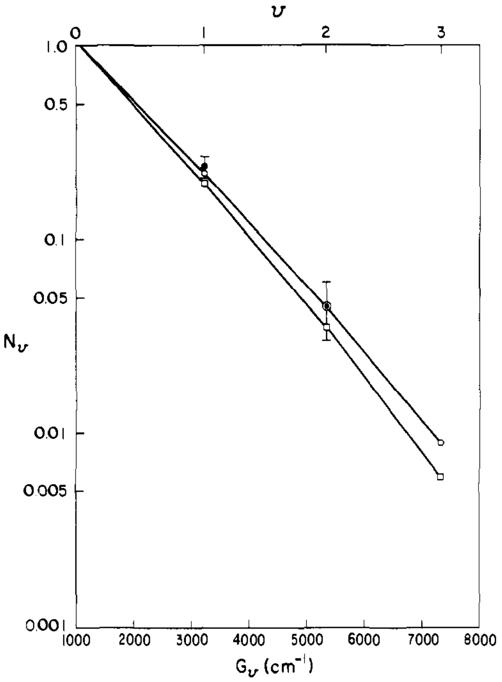

Figure 2. Vibrational energy distribution of the CO product formed by the photolysis of 3,5-cycloheptadienone at 249 nm: (●) experimental data; (○) distribution calculated with an available energy E = 100 kcal/mol; (□) distribution calculated with an available energy E = 90 kcal/mol.

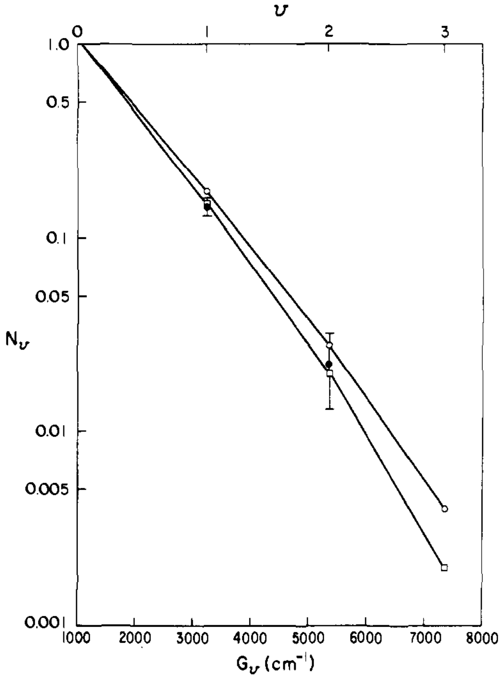

Figure 3. Vibrational energy distribution of the CO product formed by the photolysis of 3,5-cycloheptadienone at 308 nm: (●) experimental data; (○) distribution calculated with an available energy E = 80 kcal/mol; (□) distribution calculated with an available energy E = 70 kcal/mol.

Discussion

Following the original observation by Chapman et al.[11] that CHD undergoes facile photochemical decarbonylation, more

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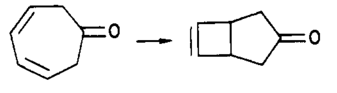
detailed studies of the photochemistry of this species in solution have been carried out by Schuster and co-workers.[9,12] They concluded that the direct photolysis of CHD yields CO and hexatriene (eq 1) in their ground electronic states, most likely via a concerted, cheletropic reaction. The photofragmentation was found to occur from the lowest excited singlet state, S_1, and if a higher excited singlet, S_2, was prepared by irradiation with $\lambda < 300$ nm, rapid radiationless decay to S_1 occurred prior to dissociation. Semiempirical electronic structure methods have been used to investigate the nature of CHD's excited states, and it was found[13] that the excited singlet states accessible via UV photoexcitation were all characterized by interactions of varying extent between the diene and carbonyl chromophores, i.e., zeroth order (n,π^*) and (π,π^*) states are mixed. The triplet-state photochemistry of CHD has been studied by using sensitization techniques.[12] The chemistry occurring from the triplet manifold was found to be qualitatively distinct from that observed on direct photolysis. Exclusive photoisomerization, eq 3, was observed in the former case, while fragmentation, eq 1, was the dominant process in the latter. The observations summarized here allow some preliminary conclusions to be drawn regarding the photophysics of CHD relevant to the present studies. Triplet states do not play a significant role in the chemistry of CHD induced by direct photoexcitation. The photochemistry of CHD is initiated predominantly from its lowest excited singlet state. Since the products are formed in their ground electronic states,[14] the photoreactive singlet must undergo a radiationless transition to the ground electronic state at some point. Other considerations suggest that the most favorable geometry for this radiationless transition is one where the vertical energy difference between the two coupled surfaces is minimized[15] (cf., the "energy gap" law for radiationless transitions). This is likely to be a geometry corresponding to an energy maximum, e.g., the transition state, on the ground-state surface. We will subsequently consider our experimental results in terms of the photophysical model outlined above.


(3)

The pressure-dependent rise time of the transient laser absorptions observed here (see above) is due to rotational relaxation of the nascent CO product. Our CO laser oscillates only on a few low J transitions in a given vibrational band: typically P-(9)-P(14). If a significant fraction of the nascent CO is formed in higher J states, collision-induced rotational relaxation is required in order to detect the CO molecules by laser absorption. The rise time of the laser absorption signal provides a qualitative indication of the extent of rotational excitation in the CO product. The absorption rise times observed here are comparable to those found in our previous work with 3-cyclopentenone.[5,6] This suggests (but does not require) that the CO product rotational energy distributions are likely to be comparably excited in both cases. The fact that pressure-dependent rise times are observed at all indicates only that the nascent CO rotational temperature is greater than 300 K or, perhaps, is non-Boltzmann. Further measurements will be required to accurately characterize the rotational energy distributions of the CO product of CHD or 3-cyclopentenone photolyses.

The nascent CO photoproduct obtained via the UV excitation of CHD is vibrationally excited. The observed vibrational distributions depend on excitation wavelength (see Figure 1–3). Each distribution can be characterized by a vibrational temperature, T_v, which is determined by the slope of the best straight line through the ($\ln N_v$ vs. v) data. We find T_v = 2600, 2000, and 1600 K for UV excitation wavelengths of 193, 249, and 308 nm, respectively. Somewhat more insight regarding the dissociation dynamics of CHD can be obtained by comparing the experimental CO vibrational energy distributions with distributions computed on the basis of a physical model. A statistical model is particularly useful in this regard since it represents a well-defined limiting case. Specificially, if dissociation occurs so that all degrees of freedom corresponding to vibration, relative rotation, and translation of the developing fragments are strongly coupled, the CO product vibrational energy distribution $f(\epsilon;E)$, is given by eq 4, where ϵ is the CO vibrational energy and E is the total available energy.[5,6,16,17] In eq 4, $N_C(\epsilon)$ is the CO vibrational density of states

$$f(\epsilon;E) = \frac{N_C(\epsilon)\int_0^{E-\epsilon} P_r(E-\epsilon-\epsilon_t)\cdot\epsilon_t^{1/2}\,d\epsilon_t}{\sum\limits_{\epsilon=0}^{E} N_C(\epsilon)\int_0^{E-\epsilon} P_r(E-\epsilon-\epsilon_t)\cdot\epsilon_t^{1/2}\,d\epsilon_t} \qquad (4)$$

at energy ϵ, and $P_r(E)$ is the number of states for all other internal and relative rotational degrees of freedom at energy E. For a given choice of available energy, eq 4 can be evaluated by using a semiclassical approximation for ro-vibrational state counting.[18,19] Some calculated vibrational distributions are shown in Figures 1–3. The maximum energy which may be statistically partitioned among the dissociation products' various degrees of freedom is the reaction exoergicity, $E \approx h\nu - \Delta H^\circ_1$, where $h\nu$ is the energy of an UV excimer laser photon and ΔH°_1 is the enthalpy change for eq 1. Using standard thermochemical estimation methods,[20] we find the reaction exoergicity is E = 132.5, 99.3, and 77.5 kcal/mol at 193, 249, and 308 nm, respectively. As illustrated in Figures 1–3, the experimentally determined CO vibrational energy distributions are reproduced quite well by calculated distributions assuming energies on the order of the full exoergicity, $E = h\nu - \Delta H^\circ_1$, to be available for statistical partitioning among all product modes. Based on the nascent CO vibrational energy distributions, we thus conclude that in the fragmentation of CHD, the full reaction exoergicity is available to be statistically partitioned among the products' degrees of freedom. In our studies of the dissociation of 3-cyclopentenone, eq 2, significantly different conclusions were reached.[5,6] In the case of (2), the measured CO vibrational distributions were consistent with a statistical model only if the available energy was chosen to be substantially *less* than the reaction exoergicity. In fact, for reaction 2, the available energy was determined to be the transition state's non-fixed energy, $h\nu - E_0$. Results for reactions 1 and 2 are compared in Table I. These results provide a good indication that more energy is partitioned into product vibrational modes in the dissociation of CHD, eq 1, than in the dissociation of 3-cyclopentenone, eq 2. We conclude *there are fundamental differences in the fragmentation dynamics for these two reactions.* Possible origins for these differences are now considered.

Table I. Comparison of Results on Energy Disposal to CO in the Photoactivated Fragmentation of 3,5-Cycloheptadienone and 3-Cyclopentenone

	3,5-cycloheptadienone			3-cyclopentenone		
λ, nm	193	249	308	193	249	308
$E_x{}^a$ (kcal/mol)	132.5	99.3	77.5	133	99.8	78
$E_{nf}{}^b$ (kcal/mol)	*c*	*c*	*c*	97	63.8	42
T_v (K)	2600	2000	1600	2900	1800	640
E^d (kcal/mol)	130-140	100	70-80	100	60-70	<40

[a] Reaction exoergicity; $E_x = h\nu - \Delta H^\circ$. [b] Non-fixed energy of the transition state: $E_{nf} = h\nu - E_0$. [c] No value of E_0 for the fragmentation of 3,5-cycloheptadienone has been reported. [d] Energy required to fit experimental CO vibrational energy distribution by using eq 4.

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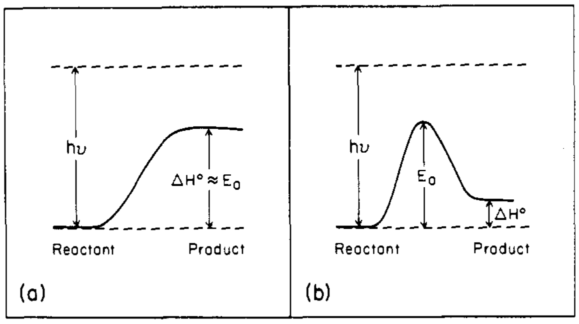
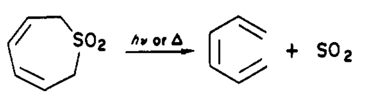


Figure 4. Model potential energy surfaces for the dissociation of 3-cyclopentenone and 3,5-cycloheptadienone: (a) type 1 surface; (b) type 2 surface (see ref 1).

Since both fragmentation reactions 1 and 2 are photoactivated, it is conceivable that differences in their energy disposal dynamics are photophysically based. For example, (1) might correspond to a direct fragmentation via a repulsive excited-state surface while (2) might represent a predissociation. This is an implausible source of the discrepancy on several grounds. For both CHD[13] and 3-cyclopentenone,[21] different electronic transitions are excited by irradiation at 193 and 308 nm. However, the manner in which energy is partitioned to product vibrations is found to be a consistent and relatively simple function of available energy for each ketone, showing no discontinuities that might be ascribed to electronic state dependent energy disposal. By fitting experimental vibrational distributions using eq 4, we find that the required available energy, E, is in all cases larger than would be anticipated if products were formed (i.e., vibrationally decoupled from one another) on an excited state potential surface. The formation of ground-state products in the photodissociation of CHD and 3-cyclopentenone indicates that radiationless decay from an excited singlet state to some point on the ground electronic state surface occurs in both cases. The most probable geometry for this radiationless transition is in the vicinity of the energy maximum ("transition state") on the ground-state surface since this is likely to correspond to the geometry where the vertical energy difference between the two coupled surfaces is minimized.[15] Thus, the photophysics of CHD and 3-cyclopentenone appear to be at least qualitatively similar. Some other basis for the observed difference in energy disposal dynamics between (1) and (2) should therefore be considered. It might be suggested that this difference arises due to non-statistical energy partitioning among product vibrational modes in the case of (1) and/or (2). Such effects have, of course, been previously observed in photofragmentation reactions.[22,23] Our observation that a single statistical energy disposal model fits the CHD results between 193 and 308 nm and that a single (but different) statistical model fits the 3-cyclopentenone results over the same wavelength range suggests that either any non-statistical effects occur to the same relative extent over this range of energy or that non-statistical effects are not operative. The unimolecular decay of some small molecules has been studied by using trajectory calculations. Non-RRKM lifetime distributions have been observed, but the relative importance of such non-statistical behavior was found to be strongly dependent on the internal energy of the decomposing species.[24,25] If analogous internal energy effects on non-statistical energy disposal obtain, it would appear that statistically based energy disposal models are the most straightforward means to characterize our observations on CHD and 3-cyclopentenone. Differences in energy disposal dynamics for (1) and (2) might be ascribed a priori to differences in the gross shape of the potential surfaces for these reactions. Our previous studies on the dissociation dynamics of 3-cyclopentenone[5,6] indicated that product vibrational energy distributions for (2) are determined at the transition state for the reaction (see Table I), i.e., only the non-fixed energy of the transition state, $h\nu - E_0$, is available to be statistically distributed among the products' vibrational modes. The ground-state potential surface for (2) is a type 2 surface (Figure 4b) for which the activation barrier has been experimentally determined[26] to be ca. 51 kcal/mol. If the dissociation of CHD occurred on a type 1 surface (Figure 4a), the CO product vibrational energy distribution should be in accord with an energy disposal model assuming the full reaction exoergicity, $E = h\nu - \Delta H° = h\nu - E_0$, to be available for statistical partitioning among all the products' degrees of freedom. Thus, if reaction 1 had no barrier in excess of its endothermicity, an identical energy disposal model could be invoked to explain our observations in the case of (1) *and* (2). Although no measurement of the activation barrier for (1) has been reported, some considerations suggest that it must be significant. If CHD had no barrier to decomposition, then $E_0 \approx \Delta H°_1 \approx 15.5$ kcal/mol and its lifetime at room temperature would be $\lesssim 40$ ms.[27] However, CHD is stable for at least several hours at 300 K. Therefore $E_0 > \Delta H°_1$. Sulfones I and II undergo photochemically and thermally activated fragmentations in analogy to (1) and (2). I and II have comparable dissociation barriers.[28]



(5)

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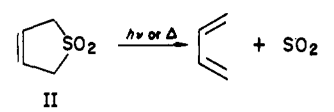
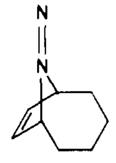


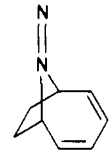
(6)

II

Diazenes, being isoelectronic with ketones, represent useful analogies, and it has been reported[29] that III undergoes fragmentation significantly faster than IV. These analogies all serve



III



IV

to suggest that the activation barrier for (1) is at least as large as that for (2), i.e., $E_0(1) \geq 51$ kcal/mol. It can be concluded that the ground-state potential surface for (1) is not a type 1 surface. We note that if CHD has a barrier to dissociation, $E_0 \geq 51$ kcal/mol, the non-fixed energy of the transition state for (1) is $E_{nf}(1) \leq 96.5$, 63.3, and 41.5 kcal/mol for photoactivation at 193, 249, and 308 nm, respectively. CO vibrational energy distributions calculated by using eq 4 with $E = E_{nf}(1)$ are substantially colder than those observed experimentally, laying well below the error bars shown in Figures 1–3. Since the exit channels for both (1) and (2) lay on the ground electronic state surface (i.e., radiationless decay precedes product formation, cf., discussion above), differences in the energy disposal dynamics for the two reactions apparently must arise from differences in how the developing products' internal and external degrees of freedom are coupled. Our results with 3-cyclopentenone indicate that only the non-fixed energy of the transition state ($h\nu - E_0$, Figure 4b) is statistically partitioned among the products' vibrational modes. The release of potential energy, $E_0 - \Delta H°$, in the exit channel is principally to the products' relative translational motion. In

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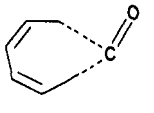
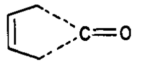
the case of CHD, the full reaction exoergicity, $h\nu - \Delta H^\circ$, is statistically partitioned among the products' internal and external degrees of freedom. For this to be the case, all of the developing products' degrees of freedom must be effectively coupled (i.e., exchanging energy) well into the exit channel.

We now consider the possibility that the dynamical effects which couple the developing products' degrees of freedom in qualitatively different ways for (1) and (2) have a *mechanistic* origin. It is possible, for example, that both (1) and (2) are concerted, cheletropic reactions subject to propensity or selection rules based on the conservation of electronic state symmetry[7,8,28] (i.e., the Woodward–Hoffmann rules). The selection rules pertaining to reactions on the ground electronic state surface are most relevant for our considerations if the exit channels for (1) and (2) are on this potential surface (vide supra). These rules predict that the allowed mode of dissociation for CHD on the ground-state surface is nonlinear (non-least motion), V, while the corresponding allowed dissociation mode for 3-cyclopentenone is linear (least motion), VI. In the fragmentation of 3-cyclopentenone, energy in the reaction coordinate is channeled primarily to the relative translational motion of the CO and butadiene products. In fact our results with this system indicated that essentially all of the potential energy released in the exit channel appears as the kinetic energy of separation of the products.[5,6] In this case, internal modes of the developing products are uncoupled from one another in the exit channel. A different situation may hold for the nonlinear concerted dissociation of CHD. The reaction coordinate can be considered as a combination of bending and stretching vibrations which correlate with product relative rotational, as well as translational, motion. Any impulsive energy imparted to the CO carbon near the transition state may excite CO rotational and orbital motion to some extent. This suggests that, on average, the products formed in the dissociation of CHD remain in closer proximity for a longer period of time than in the case of 3-cyclopentenone. Under these conditions, vibration–rotation coupling, e.g., Coriolis forces, may provide an effective means to couple *all* the developing products' degrees of freedom well into the exit channel, resulting in complete randomization of available energy. Since, in the least motion dissociation of 3-cyclopentenone, product rotational motion is not strongly excited, no mechanism exists for effectively coupling the developing products' degrees of freedom in the exit channel and the relatively rapid, impulsive separation of the products minimizes the time over which any such coupling could occur. Vibration–rotation coupling typically represents only a perturbation on energy levels. This suggests that rather than randomizing the complete reaction exoergicity, such coupling would more likely make available to the developing products' internal modes only a fraction of the potential energy released in the exit channel for CHD's dissociation. The result would be a CO product vibrational energy distribution consistent with an available energy only somewhat greater than the transition state's non-fixed energy and significantly less than the full reaction exoergicity. In this case, substantial product rotational excitation would thus be anticipated. Our results indicate that the full reaction exoergicity is statistically partitioned among the various degrees of freedom of the CHD dissociation products and that the products of CHD and 3-cyclopentenone fragmentation are rotationally excited to similar extents. Thus, either vibration–rotation coupling *dominates* the dynamics of the nonlinear cheletropic dissociation of CHD well into the exit channel or an alternative mechanistic model must be invoked.

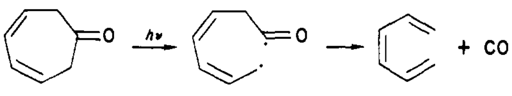


V



VI

Some evidence indicates the fragmentation of 3-cyclopentenone, (2), is a concerted process.[5,6,26,30] No such evidence has been reported in the case of CHD, (1). This raises the possibility that CHD may dissociate via a biradical intermediate, eq 7. In this case our experimental results on CHD would reflect the dissociation dynamics of the biradical, VII. The lifetime of VII can be estimated by using quantum-RRK theory.[31] We find that for $\lambda \leq 308$ nm, this lifetime is ca. 10^{-13}–10^{-12} s, if the barrier to decomposition is ~ 3 kcal/mol. If internal energy in VII is randomized within this lifetime, significant excitation of the biradical's torsional and bending modes can be expected. This may lead to the activation of product rotational and orbital motion early in the exit channel. Again, however, extensive vibration–rotation coupling is required to statistically partition the full reaction exoergicity among all the products' degrees of freedom. As in the case of the concerted mechanism described above, this vibration–rotation coupling must persist well into the exit channel. We conclude that, regardless of which of the two mechanisms outlined here is operative, the products of CHD fragmentation are strongly coupled in the exit channel. At present, there is no compelling reason to believe that the biradical mechanism, (7), is more plausible than the non-least motion concerted mechanism for the dissociation of CHD.



VII

(7)

The salient features of the model suggested here for the fragmentation dynamics of photochemically activated CHD and 3-cyclopentenone can be summarized as follows:

(i) Excitation of either ketone between 193 and 308 nm yields the lowest excited singlet state [which may be considered to be predominantly (n,π^*)] either directly or via rapid internal conversion from higher excited singlet states.

(ii) The $^1(n,\pi^*)$ state thus formed undergoes radiationless decay to the ground electronic state. The most likely geometry for this process is one corresponding to an energy maximum on the ground-state surface, i.e., a geometry corresponding to the transition state for fragmentation. Therefore, the exit channel for the reaction of either ketone is on the ground-state potential surface.

(iii) In the case of 3-cyclopentenone, the reaction coordinate on the ground-state surface corresponds to a linear or least motion cheletropic dissociation. The developing products separate impulsively from one another in the exit channel. Therefore, the two fragments are vibrationally decoupled from one another early in the exit channel, i.e., near the transition state. As a result, only the non-fixed energy of the transition state is available for (statistical) partitioning among the developing products' vibrational modes.

(iv) In the case of CHD, the reaction coordinate on the ground-state surface corresponds to a nonlinear (non-least motion) concerted dissociation or a stepwise fragmentation process, involving a biradical intermediate. To the extent that the relative orbital and rotational motion of the developing fragments is excited, the products separate from one another more slowly than in the case of 3-cyclopentenone. All the degrees of freedom of the developing products are effectively coupled by vibration–rotation interactions as the dissociation of CHD occurs. This coupling can persist relatively far into the exit channel since the fragments tend to remain in closer proximity to one another than in the case of 3-cyclopentenone. As a result, virtually the entire reaction exoergicity is available to be statistically partitioned among all the products' vibrational modes.

The model we have described accounts for differences in the dissociation *dynamics* between CHD and 3-cyclopentenone in terms of differences in the *mechanisms* of the two reactions, (1) and (2). Our results demonstrate that there are significant differences in the energy disposal dynamics associated with these two fragmentation processes. Specifically, the entire reaction exoergicity is available to product vibrational modes in (1) while

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only the non-fixed energy of the transition state is available in (2). The mechanistically based model suggested here to account for these results is certainly not the only one capable of doing so. It is, however, consistent with some of the limited available data on the dissociation dynamics of polyatomic molecules and the basic trends observed in the photochemistry and photophysics of polyatomics. We are presently studying energy disposal dynamics in the fragmentation reactions of several other cyclic ketones. The data thus obtained will be useful in evaluating further the mechanistic/dynamical model outlined here.

Conclusion

We have measured the nascent vibrational distribution of the CO product obtained by photolyzing 3,5-cycloheptadienone at 193, 249, and 308 nm. The measured distributions are consistent with a statistical model where the full reaction exoergicity is available for partitioning among all the products's degrees of freedom. This indicates the developing fragments are strongly coupled well into the exit channel. These findings are contrasted with our results on the dissociation dynamics of 3-cyclopentenone where the product vibrational energy distribution is determined at the transition state, i.e., the fragments are vibrationally decoupled from one another in the exit channel so that only the transition states' non-fixed energy is available to the products' vibrational modes. A mechanistically based model for the differences in energy disposal dynamics between 3,5-cycloheptadienone and 3-cyclopentenone is suggested.

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Registry No. CO, 630-08-0; 3,5-cycloheptadienone, 1121-65-9; 3-cyclopentenone, 14320-37-7.

Detection of the Prototype Phosphonium (CH_2PH_3), Sulfonium (CH_2SH_2), and Chloronium (CH_2ClH) Ylides by Neutralization–Reionization Mass Spectrometry: A Theoretical Prediction[1]

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Abstract: Ab initio molecular orbital calculations with polarized basis sets and incorporating electron correlation have been carried out on the prototype phosphonium (CH_2PH_3), sulfonium (CH_2SH_2), and chloronium (CH_2ClH) ylides, and the corresponding ylidions ($CH_2PH_3^{+\cdot}$, $CH_2SH_2^{+\cdot}$, and $CH_2ClH^{+\cdot}$). The results are discussed within the context of the detectability of reactive neutral molecules by neutralization–reionization mass spectrometry.

In a recent communication, McLafferty et al.[2] demonstrated how combination of the techniques of neutralization[3] followed by reionization[4] in a tandem mass spectrometer[5] gives rise to a powerful, new mass-spectrometric procedure: neutralization–reionization mass spectrometry (NRMS). NRMS may in particular be used to study unstable and reactive neutrals whose parent ions are stable (e.g., $CH_2{=}CHOH/CH_2{=}CHOH^{+\cdot}$). In the ideal experiment, the stable parent ion is generated uniquely and neutralized, and the neutral which is produced is reionized and characterized by using collisionally activated dissociation (CAD). Observation of a CAD spectrum which coincides with that of the parent ion demonstrates the stability of the neutral within the time frame ($\sim 10^{-6}$ s) of the NRMS experiment.

For some time now, our theoretical studies have been concerned with systems which turn out to be ideally suited for examination by the NRMS procedure, viz. stable ions whose neutral counterparts are either unstable or reactive.[6,7] In this paper we show how theory may be used to predict whether a particular neutral of this type is likely to be "detectable" by NRMS. For this to be the case, *the energy of the vertically neutralized species should be lower than that of transition structures for subsequent rearrangement or fragmentation.* We illustrate the approach with calculations on the prototype phosphonium (CH_2PH_3), sulfonium (CH_2SH_2), and chloronium (CH_2ClH) ylides.[8]

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