internal energy of the parent ion can have important effects on the photodissociation process. Similar conclusions have been reached in earlier studies where collisional cooling of the parent ions had an observed effect on the photodissociation thresholds.[22] In addition, a previous study by Dunbar and co-workers indicated that *n*-butylbenzene ion yields fragments m/e 91 and 92 upon photodissociation, with the ratio of 91/92 increasing with increasing internal energy of the parent ion.[23]

Conclusion

The study of $FeC_5H_6^+$ and its reaction with several small alkanes reveals some very interesting features. The presence of a cyclopentadiene ligand on Fe^+ has a dramatic effect on the reactivity of Fe^+. The rearrangement of Fe^+–cyclopentadiene to cyclopentadienylhydridoiron enhances reactivity and changes the reaction mechanism. While Fe^+ does not react with ethane, $FeC_5H_6^+$ reacts readily. $FeC_5H_6^+$ also reacts rapidly with propane and *n*-butane to form cyclopentadienylallyliron ion and cyclopentadienyl(methylallyl)iron ion, respectively.

Photodissociation threshold measurements yield $D°(Fe^+–C_5H_6) = 55 \pm 5$ kcal/mol. From this, the reaction exothermicity of Fe^+ dehydrogenation of cyclopentene is calculated to be 33 ± 5 kcal/mol. Some of this energy, along with a fractional portion of the kinetic energy from the laser-generated Fe^+, might reside with the ionic product, $FeC_5H_6^+$, and affects subsequent kinetic behavior. Correct kinetic data can only be obtained by removing the excess energy with background argon.

Photodissociation studies on cyclopentadienylallyliron ion shows that effects on product branching ratios due to internal energy of the parent ion are observed. Without removing the internal energy, the higher energy process forming $FeC_6H_6^+$ is favored. By removing the internal energy with a high pressure of background argon, the lower energy dehydrogenation process forming $FeC_8H_8^+$ is favored.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this research and the National Science Foundation (CHE-8612234) for continuing support of the FTMS.

---

[22] Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537.

[23] Chen, J. H.; Hays, J. D.; Dunbar, R. C. *J. Phys. Chem.* **1984**, *88*, 4759.

Dynamics of the Thermal Dissociation of Unsaturated Cyclic Ketones: Nascent Vibrational Energy Distributions in the Products

C. J. S. M. Simpson,*,† J. Price,† G. Holmes,† W. Adam,‡ H.-D. Martin,§ and S. Bish§

Contribution from The Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, England, Institut für Organische Chemie, der Universität Würzburg, D-8700 Würzburg, West Germany, and the Institut für Organische Chemie I der Universität, Universitätsstrasse 1, D-4000 Düsseldorf, West Germany.

Received June 20, 1989. Revised Manuscript Received December 1, 1989

Abstract: It has been found that in thermal dissociation of both norbornenone and 3-cyclopentenone the CO is formed with less than half its statistical share of the energy released from the transition state. We have used (VV) coupling between the products, 1,3-cyclohexadiene and butadiene, respectively, to probe their nascent vibrational energy. They are both born vibrationally excited. It seems that much of the energy released appears as vibrational energy of these molecules. In the transition state the CO group must have a bond length close to that of the free molecule. These results do not permit a decision between symmetric and asymmetric bond cleavage. However, separate experiments in which the rotational distribution has been measured establish that the dissociation does not occur by symmetric bond rupture.

A great deal of research has been conducted in order to discover whether thermal and photochemical dissociation of keto and azo compounds proceeds by the synchronous cleavage of both bonds to the CO or the N_2 groups or sequentially.[1-3] The sequential mechanism has been proved for an unsymmetrical azo compound $CH_3N{=}NR$ by the discovery that in the photochemical dissociation the radical R is formed before the CH_3 and the N_2.[4] However, this is not so surprising considering that the CH_3–N bond is about twice as strong as the R–N bond.[4] Synchronous cleavage is more likely for symmetrical compounds such as $CH_3N{=}NCH_3$, H_2CO, and symmetrical cyclic compounds such as

and

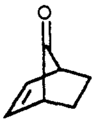
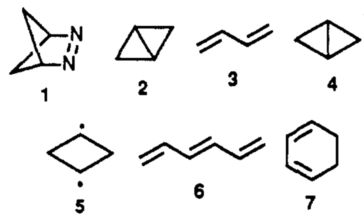


Chart I



Many years ago Bauer suggested that synchronous cleavage could lead to highly vibrationally excited N_2 and CO molecules because of the large changes in the N–N and C–O bond lengths.[5] As pointed out by Engel and co-workers,[6] the degree of vibrational

---

† Oxford University.

‡ Universität Würzburg.

§ Institut für Organische Chemie I der Universität.

[1] Wentrup, C. *Reactive Molecules*; John Wiley and Son: New York, 1984.

[2] Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[3] Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. J. *J. Am. Chem Soc.* **1983**, *105*, 7102.

[4] Adams, J. S.; Barton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 7935.

[5] Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 3688.

0002-7863/90/1512-5089$02.50/0 © 1990 American Chemical Society

excitation of the N_2 depends not on the change in the N–N bond length between the azo compound and N_2 but on the change in length between the transition state and N_2. We made similar comments for the thermal dissociation of cyclic carbonyl compounds.[7] The other factors that Engel and co-workers consider to be important are the internal energy available in the transition state and the impulsive force in the exit channel, while we have suggested that the CO group may become decoupled from the parent molecule before the energy is released during the rearrangement of the organic fragment.

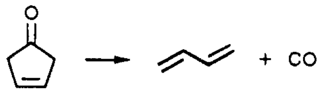
There have not been very many direct measurements of energy partitioning in the dissociation of azo compounds. One example is the photolysis of $CH_3N{=}NCH_3$ with transient CARS spectroscopy to measure vibrational energy in the products, by Engel and co-workers.[6] They found that only a small fraction of the 16 800-cm^{-1} energy released after photolysis at 355 nm goes into vibration of N_2, to give about 84% in $v = 0$ and 16% in $v = 1$, with little energy going into N_2 rotation. They suggest that $S_1 \rightarrow S_0$ internal conversion takes place in about 10^{-11} s, followed by the dissociation of the highly energized $S_0{}^*$ molecules by a diazenyl intermediate, though they had no direct proof of this.

Dougherty and co-workers[8] have investigated the thermal decomposition of **1** to give **2** and **3** (Chart I). They considered that **3** is formed from vibrationally excited **2**, provided that **4** is not first deactivated. By measuring the ratio of **3** to **2** as a function of pressure of added gas they calculated how fast **4** must isomerize. From an RRKM calculation they concluded what the energy must be in **4**. Since this was only 13 kJ mol^{-1} less than the difference between the energies of the transition states for the dissociation of **1** and the isomerization of **2**, they decided that very little energy goes into the N_2. From this they concluded that N_2 loss occurs in a stepwise fashion, via an intermediate diazenyl diradical. A minor criticism of this argument is that slightly more energy must have been available to go into the N_2 since there was some energy in the first transition state for the decomposition of **1**. More serious is the question of whether lack of vibrational energy in the N_2 conclusively proves a diazenyl diradical mechanism. In the transition state the C–N bonds might be greatly stretched and the N–N bond greatly shortened. If little energy were released into the N_2 on the formation of a diradical and N_2, then vibrationally and rotationally unexcited N_2 might be formed with the major energy release occurring on ring closure of **5** or the formation of **3**. It may be that the absence or presence of rotational energy in the N_2 is a clear indication of synchronous bond cleavage.

The two other molecules referred to by Engel[6] for ground-state dissociation are H_2CO[9] and 3-cyclopentenone.[10]

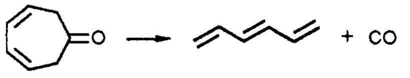
The CARS experiment on the photodissociation of H_2CO[9] showed the production of vibrationally excited H_2 for photolysis at λ near 340 nm. For photolysis at $\lambda \leq 335$ nm fragmentation to H + HCO is important. This raises the question as to whether photochemical and thermal dissociation processes need follow the same paths. It may be that when very large amounts of energy are deposited into the electronic ground state many vibrational modes become highly excited. For example, in CO_2 the antisymmetric stretching modes, symmetric stretching modes, and bending modes may be excited and similar conditions may apply to other molecules such as $(CH_2)_2CO$, C_2O_2, and H_2CO.

Rosenfeld and co-workers[10] photolyzed 3-cyclopentenone at 193, 249, and 308 nm and measured the vibrational energy in the CO produced in process. They found that the vibrational energy content increased as the energy of the photon was increased. They presumed that following the electronic excitation extremely rapid relaxation occurs to give highly excited molecules in their electronic ground state, giving the total energy in the molecule prior to dissociation as $h\nu$.


(1)

To account for their results they first tested the hypothesis that the energy $h\nu - \Delta H$ is partitioned statistically between the products, where ΔH is the difference in heats of formation of 3-cyclopentenone and butadiene. This predicted far too much vibrational energy in the CO. They then assumed that only the energy in the transition state is so partitioned. These values are given by $h\nu - E_A$, where E_A is the activation energy for thermal dissociation. The calculated distributions of vibrational energy agreed with those measured quite well, though for dissociation at 308 nm there was considerably less energy in the CO than they calculated. They assumed that the rest of the energy, $E_A - \Delta H$, that is released is not partitioned into vibration but appears largely as translational energy.

The hypothesis that only the energy $h\nu - E_A$ is partitioned statistically into the vibrations of the products is certainly not generally true, for Rosenfeld and co-workers found that it does not apply to the photochemical dissociation of 3,5-cycloheptadienone.[11]


(2)

They did not know E_A and so could not calculate the values of $h\nu - E_A$. However, we have measured this dissociation energy using a shock tube.[7] At 255 ± 10 kJ mol^{-1} it is slightly greater than that for the dissociation of 3-cyclopentenone, which is 214 ± 1 kJ mol^{-1}.[7,12] This implies that the values of $h\nu - E_A$ are smaller than for 3-cyclopentenone, and so if this were the energy partitioned into vibration, the CO would be less vibrationally excited in process 2 than in process 1. In fact the CO is born much more highly excited, the distributions being close to those expected for the statistical partitioning of all of the available energy, $h\nu - \Delta H$.

According to this model there should be a very large change in the translational energy of the CO between these two dissociation processes. For the dissociation of 3-cyclopentenone they postulate that the energy $E_A - \Delta H$, which is not partitioned into vibration, appears largely as translational energy of the products. This is about 150 kJ mol^{-1}. However, for the dissociation of 3,5-cycloheptadienone, it is proposed that all the available energy, $h\nu - \Delta H$, is partitioned statistically between the vibrational modes of **6** and CO and the rotational and translational motions of these molecules, resulting in much lower translational energies.

We have measured rate constants for the thermal decomposition of 3,5-cycloheptadienone, 3-cyclopentenone, and norbornenone (bicyclo[2.2.1]hept-2-en-7-one) as dilute mixtures in Ar using a shock tube and a continuous wave CO probe laser. Under the conditions used, the organic product molecules **6**, **3**, and **7** are vibrationally relaxed to the equilibrium condition by the Ar within a few microseconds, but the Ar does not relax vibrationally excited CO significantly during the observation time. The CO is relaxed by the organic products, and we measured the rate constants for these processes. We then chose conditions such that the CO is not relaxed significantly for the first portion of the observation time but is relaxed to the equilibrium condition by the end of this time. This enabled us to compare the nascent vibrational condition of the CO with the equilibrium distribution and with that calculated for the statistical distribution of the energy $E_A - \Delta H$.

We found that the CO($v = 1$) formed from the thermal decomposition of both norbornenone and 3-cyclopentenone is about half that calculated for the statistical distribution and is less than the equilibrium distribution at the translational temperature. However, for 3,5-cycloheptadienone the nascent vibrational dis-

---

[6] Holt, P. L.; McCurdy, K. E.; Adams, J. S.; Burton, K. A.; Weisman, R. B.; Engle, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 2180.

[7] Buxton, J. P.; Simpson, C. J. S. M. *Chem. Phys.* **1986**, *105*, 307.

[8] Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 4211.

[9] Peatal, M.; Debarre, I.; Marie, J.-M.; Taran, J.-P. E.; Tramer, A.; Moore, C. B. *Chem. Phys. Lett.* **1983**, *98*, 299.

[10] Sonobe, B. I.; Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. soc.* **1984**, *106*, 4352.

[11] Sonobe, B. I.; Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 5800.

[12] Dolbier, W. R., Jr.; Fray, H. M. *J. Chem. Soc., Perkin Trans. II* **1974**, 1674.

tribution in the CO is close to the statistical distribution, which happens to be close to the Boltzmann distribution at the temperatures of the experiment.

The thermal dissociation experiments reach the same conclusion as the photochemical experiments. Rather than being born with a large amount of vibrational excitation, the CO from 3-cyclopentenone is born with little vibrational energy. This implies that in the transition state the CO bond length must have contracted to close to its value in the diatomic molecule. That the CO has less than its statistical share of the energy released on forming the products must imply that the CO is decoupled from the rest of the molecule before all of the energy is released. Rosenberg et al. assume that most of the energy $E_A - \Delta H$ goes into translation. However, it might be that the energy release on the formation of butadiene occurs after the CO has become decoupled and that vibrationally excited **3** is formed. This sequence of events for forming vibrationally excited **3** is similar to that for forming vibrationally excited **2** from **1**. Dougherty and co-workers[8] concluded that the major release of energy into the organic product takes place after the N_2 has left the transition state.

It is the objective of this paper to try to find out whether a large or a small fraction of the energy released from the transition state appears as vibrational excitation of the organic product in the thermal dissociation of norbornenone and of 3-cyclopentenone. This will help to illucidate the dynamics of the dissociation. A fuller understanding would be obtained by measuring the rotational and translational energies of the products, but unfortunately this is beyond the scope of these thermal dissociation studies.

The Nascent Vibrational Energy in the Organic Products

Since the experiments of Millikan and White[13] in 1963, use has been made of near-resonant (VV) coupling to measure the rate constants for the vibrational deactivation of one molecule by following the change in the vibrational population of the second molecule during the vibrational deactivation of a coupled system. Millikan and White used the method to determine the rate constant for the vibrational deactivation of N_2 by N_2 using 1% of CO as a monitor. The exchange reaction

$$N_2(v = 1) + CO(v = 0) \rightleftharpoons N_2(v = 0) + CO(v = 1) \qquad \Delta E = 188\ \mathrm{cm^{-1}} \quad (3)$$

has an energy mismatch of 188 $\mathrm{cm^{-1}}$, which is less than 10% of the energy transferred. For the conditions used the energy exchanged with translation and rotation is a negligible fraction of the vibrational energy in the system. They concluded that the $CO-N_2$ system has a single vibrational temperature under the conditions they employed.

We have used this method to determine rate constants for the vibrational deactivation of $N_2(v = 1)$ by n H_2 and p H_2,[14] by ^4He and ^3He,[15] by CH_4,[16] and by O_2 at low temperatures.[17] We take account of the rates of energy transfer from the N_2 and the CO and of radiative decay. We choose conditions to make the $N_2(v = 1) + M \rightarrow N_2(v = 0) + M$ the dominant process.

For the case of the deactivation of CO_2 by N_2 at low temperatures, near resonant (VV) transfer to the (001) mode with a ΔE of 18 $\mathrm{cm^{-1}}$ removes energy from the CO_2 and slows down the rate of its deactivation.[18] The deactivation occurs predominantly from the bend–stretch manifold of levels that are coupled with a common vibrational temperature.

In the present studies we have used a shock tube to induce very rapid thermal decomposition of norbornenone and of 3-cyclopentenone in the temperature ranges 900–1170 and 1330–1480 K, respectively.

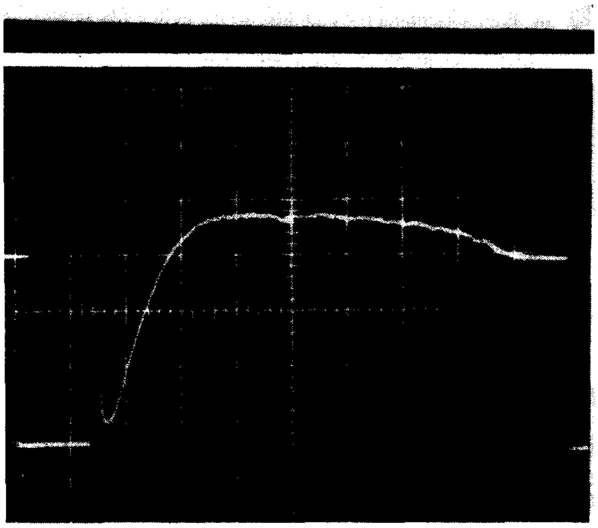


Figure 1. Laser gain curve for ($v = 4 \rightarrow 3$) $P(10)$ for 4% norbornenone in CO (P = 42 Torr, T = 1234 K, time scale = 20 μs per main division). The spike near the start of the trace shows the time origin for shock heating.

For polyatomic molecules at temperatures of above 1000 K, the density of vibrational states is high and coupling between vibrational modes fast. To a good approximation the molecule can be taken to have a vibrational temperature, with vibrational deactivation taking place via the lowest mode.[19,20]

The high density of states in the vibrationally excited products makes it very likely that there are states close in frequency to that of CO to which near-resonant (VV) transfer will occur with a larger rate than that for their (VT) deactivation by CO.[19,20] How close to a pseudoequilibrium condition there will be between the vibrationally excited products M* and CO* will depend upon the ratio of the rate constants for vibrational coupling and deactivation.

In due course the CO, which is vibrationally unexcited behind the shock front, will be driven to vibrational equilibrium with the translational temperature, T_e. On the time scale of these experiments this relaxation is due only to the product molecules, M. We have measured the rate constants for this process and chose conditions such that the relaxation takes say 100 to 400 μs. At times considerably shorter than this the CO is vibrationally uncoupled to translation and is vibrationally unexcited unless it acquires vibrational energy from vibrationally excited products, M*. If M* is formed with a vibrational temperature, $T(\mathrm{v}_{\mathrm{M}_i})$, and it forms a coupled system with the CO then its vibrational temperature will fall to the coupled temperature, $T(\mathrm{v_c})$. Assuming that this is a near-resonant (VV) process and neglecting the small amount of energy transferred to translation, the coupled temperature depends on the change in energy content of M* between $T(\mathrm{v}_{\mathrm{M}_i})$ and $T(\mathrm{v_c})$, the energy content of CO at $T(\mathrm{v_c})$, and the mole fraction, m, of M in the mixture.

$$E(\mathrm{v_M})T(\mathrm{v}_{\mathrm{M}_i}) - E(\mathrm{v_M})T(\mathrm{v_c}) = \frac{1 - m}{m} E(\mathrm{v_{CO}})T(\mathrm{v_c}) \quad (4)$$

The vibrational temperature of the CO can be found from the ratio of populations in adjacent vibrational levels once a Maxwell–Boltzmann distribution has been established[21] by fast (VV) exchange processes such as

$$CO(v = 1) + CO(v = 1) \rightleftharpoons CO(v = 2) + CO(v = 0) \quad (5)$$

The vibrational energies of CO and 1,3-cyclohexadiene at this temperature can be calculated from their vibrational frequencies.[22]

---

(13) Millikan, R. L.; White, D. R. *J. Chem. Phys.* **1963**, *39*, 98.

(14) Allen, D. C.; Chandler, E. T.; Gregory, E. A.; Siddles, R. M.; Simpson, C. J. S. M. *Chem. Phys. Lett.* **1980**, *76*, 347.

(15) Maricq, M. M.; Gregory, E. A.; Wickham-Jones, C. T.; Cartwright, D. J.; Simpson, C. J. S. M. *Chem. Phys.* **1983**, *75*, 347.

(16) Maricq, M. M.; Gregory, E. A.; Wickham-Jones, C. T.; Cartwright, D. J.; Simpson, C. J. S. M. *Chem. Phys.* **1983**, *75*, 347.

(17) Gregory, E. A.; Maricq, M. M.; Siddles, R. M.; Wickham-Jones, C. T.; Simpson, C. J. S. M. *J. Chem. Phys.* **1983**, *78*, 3881.

(18) Allen, D. C.; Scragg, T.; Simpson, C. J. S. M. *Chem. Phys.* **1980**, *51*, 279.

(19) Yardley, J. R. *Introduction to Molecular Energy Transfer*; Academic Press: New York, 1980.

(20) Lambert, J. D. *Vibrational and Rotational Relaxation in Gases*; Clarendon Press: Oxford, 1977.

(21) Martin, J. P.; Buckingham, M. R.; Chenery, J. A.; Simpson, C. J. S. M. *Chem. Phys.* **1983**, *74*, 15.

(22) DiLauro, D.; Neto, N.; Califano, S. J. *Molecular Structure* **1969**, *3*, 219.

Table I. Rate Constants for CO Relaxation by Butadiene and 1,3-Cyclohexadiene

butadiene		1,3-cyclohexadiene	
T, K	k^a	*T*, K	k^a
1026	0.46	1116	0.69
1071	0.50	1185	0.99
1106	0.53	1327	1.46
1231	0.65	1428	1.86
1305	0.74	1503	2.78
1327	0.77	1640	3.07
1519	1.02		

[a] 10^{-12} cm^3 molecule^{-1} s^{-1}.

The value of $T(\mathrm{v}_{\mathrm{M}_i})$ can then be found, which gives the vibrational energy $E(\mathrm{v_M})T(\mathrm{v}_{\mathrm{M}_i})$ to satisfy (4).

If this process is repeated with a different mole fraction, *m*, of norbornenone and the same value of $T(\mathrm{v}_{\mathrm{M}_i})$ is found, then the coupled approximation is applicable, within the experimental errors of these measurements.

The coupled temperatures reached will not generally equal the equilibrium temperature, T_e. They may be above or below T_e depending upon the values of $T(\mathrm{v}_{\mathrm{M}_i})$ and the constraints of (4). If vibrationally excited CO is produced soon after the shock front and then relaxes to the equilibrium condition, this is strong evidence for the production of vibrationally excited 1,3-cyclohexadiene.

This is illustrated in Figure 1, which shows the absorption of the CO(v = 4 → 3) laser line by CO(v = 3). It is to be contrasted with our previous results in which we showed that when energy is not coupled fast out of 1,3-cyclohexadiene to CO, virtually no CO(v = 3) is produced.[7] The start of the trace shows the preshock condition where there is no absorption of the laser by CO(v = 3); the spike is due to the large density gradient at the shock front and serves as a marker for the time origin. The decrease in absorption toward the end of the trace shows that the energy transfer has led to an excess population in CO(v = 3) above that for equilibrium of the translational temperatures.

Experimental Section

For studying thermal decomposition processes a shock tube has the advantages that the heating is homogeneous, that any desired temperatures between 400 and 3000 K may be selected, and that following the jump in temperature at the shock front the conditions are nearly uniform during the observation time if dilute mixtures of reactant in a carrier gas are used. The conditions of products may be monitored as they are formed with use of a tunable continuous wave laser. In practice the time resolution of this optical detection system is controlled by the transit time of the shock-heated gas across the laser and is about 1 μs. The time resolution is not good enough to measure nascent rotational distributions but is adequate for investigating vibrational distributions. The laser and shock tube have been used for this purpose for some time.[21,23,24]

The norbornenone (bicyclo[2.2.1]hept-2-en-7-one, BCH) was prepared from the dimethyl acetate of 1,2,3,4-tetrachlorocyclopentadienone via ethylene [4 + 2] cycloaddition at 180–190 °C,[25] dechlorination of the Diels–Alder product with sodium in refluxing THF,[26] and aqueous H_2SO_4 (5%) hydrolysis at 20 °C of the resulting dimethyl acetal of BCH.[27] The norbornenone was purified to match the reported[27] physical and spectral data.

The 3-cyclopentenone (CPE) was obtained from the cyclopentadiene dimer by means of selenium dioxide oxidation[28] in aqueous dioxane at 100 °C and cracking[29] of the resulting alcohol by direct heating above 150 °C. The CPE was purified by fractional distillation to match the reported[29] physical and spectral properties.

The 1,3-cyclohexadiene and the butadiene were supplied by Aldrich. We used both C.P. grade and research grade CO and B.O.C. zero grade.

In order to determine the vibrational temperature of the CO after its excitation by the product molecules, we measured the change in the absorption of adjacent vibrational lines of the CO laser. By definition the maximum gain for the v = 3 → 2 line is

$$G_{\max}(3 \rightarrow 2) = \ln\,(1 - \Delta I_{\max}/I_0) \qquad (6)$$

where I_0 is the incident laser intensity. The gain depends upon the difference between adsorption and stimulated emission. For the *P*(10) line it is

$$G_{\max}(3 \rightarrow 2) = \left[\frac{1}{19}\right] n_{(v=3,J=9)} - \left[\frac{1}{21}\right] n_{(v=2,J=10)} \qquad (7)$$

For a Boltzmann distribution with a vibrational temperature T_v

$$n_3/n_2 = \frac{19}{21} e^{-(\omega_e - 7\omega_e x_e)hc/kT_v} \qquad (8)$$

Hence

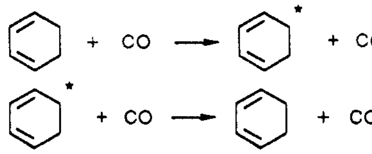
$$T(\mathrm{v}) = (hc/k)(\omega_e - 7\omega_e x_e)/\ln\,[19G_{\max}(3 \rightarrow 2)/21G_{\max}(4 \rightarrow 3)] \qquad (9)$$

The values of the gains have to be taken at the same shock conditions. Since we cannot obtain exactly reproducible conditions we plot the values of $G(3 \rightarrow 2)$ and $G(4 \rightarrow 3)$, normalize for pressure against temperature, and read off the values at selected temperatures.

Results

Norbornenone (BCH). Dissociation. We have measured rate constants for the thermal dissociation of norbornenone in Ar as a function of temperature and pressure.[7] The rate constants for its dissociation in CO are expected to be sufficiently similar for us to predict conditions that will ensure its rapid dissociation on the time scale of these experiments.

The Vibrational Excitation of the Initially Vibrationally Unexcited CO. Under our conditions, the times for the vibrational excitation of CO to the Boltzmann equilibrium condition by CO and by Ar are long on our time scale[21,30-32] and the CO is excited to equilibrium by collisions with the 1,3-cyclohexadiene present in the mixture. The process probably takes place via the formation of vibrationally excited 1,3-cyclohexadiene.


(10)
(11)

We have measured rate constants for the vibrational excitation of CO by 1,3-cyclohexadiene in an Ar carrier gas. Under these conditions (11) rather than (10) may be the rate-controlling step. The results are given in Table I.

We do not have information on the relative sizes of the rate constants for processes 10 and 11. We selected conditions in our dissociation experiments such that vibrational–translational equilibrium should be established in about 200 μs after dissociation.

The Vibrational Temperature of the CO Following the Dissociation of Norbornenone. We have measured the absorption of the v = 4 → 3 *P*(10) and the v = 3 → 2 *P*(10) lines of the CO laser following the dissociation of 4% norbornenone in CO. From our previous work on its dissociation in Ar we know that the CO is born with very little vibrational energy in v = 1 and no detectable energy in higher vibrational levels. Hence the vibrational energy in the CO must have come either from nascent vibrationally excited 1,3-cyclohexadiene, which then couples to CO, or from vibrationally excited 1,3-cyclohexadiene produced by collisions with CO, if this molecule is born vibrationally unexcited.

In Figure 2 we show a trace for the absorption of the v = 3 → 2 *P*(10) laser line following the dissociation of 4% norbornenone in CO. The small spike near the start of the trace marks the start of the dissociation. The dissociation is fast on this time scale and the rise is governed by the time for energy transfer and the es-

---

(23) Buxton, J. P.; Sohm, R. M.; Simpson, C. J. S. M. *Chem. Phys. Lett.* **1985**, *116*, 1.

(24) Aherne, A. J.; Buxton, J. P.; Chenery, J. A.; Fakhr, A.; Simpson, C. J. S. M. *Chem. Phys. Lett.* **1983**, *98*, 93.

(25) Gassman, P. G.; Marshall, J. L. *Org. Synth.* **1968**, *48*, 68.

(26) Vinh Lap, B.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979.

(27) Gassman, P. G.; Marshall, J. L. *Org. Synth.* **1968**, *48*, 25.

(28) Rosenblum, J. *J. Am. Chem. Soc.* **1957**, *79*, 3179.

(29) Hess, H. J.; Braun, H. C. *J. Org. Chem.* **1967**, *32*, 4138.

(30) Hooker, W. J.; Millikan, R. C. *J. Chem. Phys.* **1963**, *38*, 214.

(31) Millikan, R. C.; White, D. R. *J. Chem. Phys.* **1964**, *40*, 2594.

(32) White, D. R. *J. Chem. Phys.* **1964**, *40*, 2594.

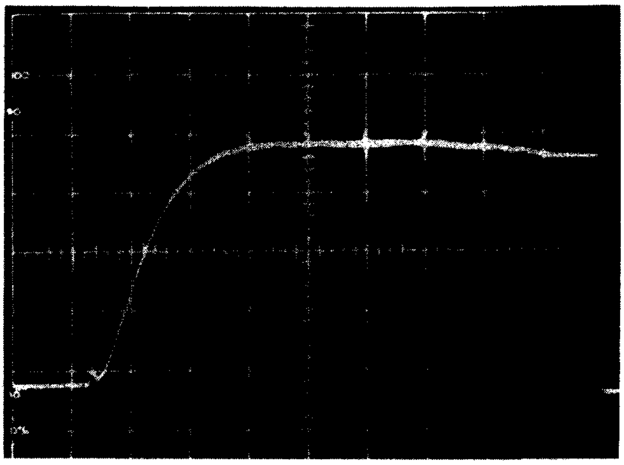


Figure 2. Laser gain ($v = 3 \rightarrow 2$) $P(10)$ for 4% norbornenone in CO (P = 45 Torr, T = 1252 K, time scale = 20 μs per main division). The schlieren spike is much smaller than in Figure 1 because of the change in vertical scale.

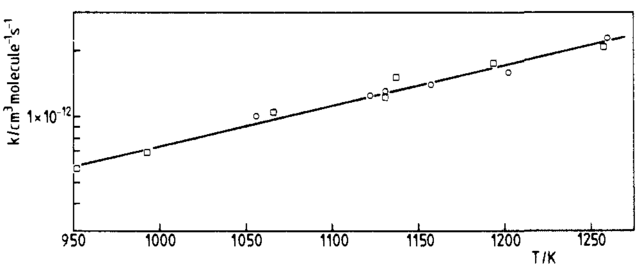


Figure 3. Rate constants for the production of vibrationally excited CO monitored with ($v = 4 \rightarrow 3$) $P(10)$, □, and ($v = 3 \rightarrow 2$) $P(10)$, ○, for 4% and 8% mixtures of norbornenone in CO.

tablishment of a vibrational temperature in the CO. This time is about half that expected from the rate constants for the vibrational excitation of CO by initially unexcited 1,3-cyclohexadiene. The absorption reaches a maximum and then decreases. This shows that the $v = 2$ level has been populated above its equilibrium value. Figure 1 shows these effects for the $v = 3$ level.

Rate constants for the production of the vibrationally excited CO have been obtained by dividing the measured relaxation time by the concentrations of 1,3-cyclohexadiene. The results are shown in Figure 3. They fall on a single line for the $v = 4 \rightarrow 3$ $P(10)$ and the $v = 3 \rightarrow 2$ $P(10)$ absorption traces. This confirms that the CO vibrational levels are in Boltzmann equilibrium with a vibrational temperature.

Values of the gains have been derived with eq 6. The results for the 4% mixture are plotted in Figure 4, from which it may be seen that the gain changes only slowly with temperature between 1000 and 1200 K. This enables us to select values of the gains for the $v = 3 \rightarrow 2$ and $4 \rightarrow 3$ laser lines at the same temperature. From these values we have used eq 9 to calculate the vibrational temperature of the CO after the transfer of energy from the vibrationally excited 1,3-cyclohexadiene and before its relaxation to equilibrium with the translational temperature. The results are given in Table II, together with the vibrational energy of CO at these temperatures.

On the assumption that the vibrational temperature of the CO is the same as that of the 1,3-cyclohexadiene after energy transfer, we have calculated the energy content in the 1,3-cyclohexadiene at these coupled temperatures. From these values we have calculated the initial temperature and energy of the 1,3-cyclohexadiene.

The validity of the coupling model that we have used can be tested by measuring the production of vibrationally excited CO following the dissociation of norbornenone in 4% and 8% mixtures in CO at the same translational temperature. If the model is correct then the two mixtures will give different coupled temperatures in accordance with eq 4, but the same nascent vibrational temperature for the 1,3-cyclohexadiene. The results in Table II show that the model works well.

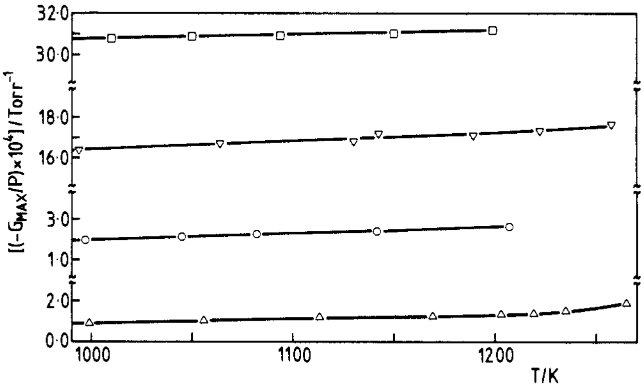


Figure 4. The variation with temperature of laser gain/pressure: ($v = 3 \rightarrow 2$) for 4% norbornenone in CO, ▽; ($v = 4 \rightarrow 3$) for 4% norbornenone in CO, △; $v = 3 \rightarrow 2$ for 8% norbornenone in CO, □; ($v = 4 \rightarrow 3$) for 8% norbornenone in CO, ○. Results plotted as $(-G_{max}/P) \times 10^4$/Torr^{-1} against T/K.

Table II. The Vibrational Temperature and Energy of CO after Energy Transfer[a]

$T(T_r)$, K	CHD, %	T_{vCO}, K	E_{vCO} (T_{vC}), kJ mol^{-1}	E_{vCHD} (T_{vC}), kJ mol^{-1}	E_{vCHD} (T_{vCHD_i}), kJ mol^{-1}	T_{vCHD_i}, K
990	4	1061	1.48	126	161	1219
990	8	1121	1.75	137	159	1209
1020	4	1102	1.66	135	175	1276
1020	8	1154	1.90	146	168	1249
1050	4	1120	1.74	139	180	1301
1050	8	1165	1.96	149	171	1262
1080	4	1138	1.83	143	187	1327
1080	8	1187	2.06	154	178	1289
1110	4	1142	1.85	144	188	1333
1110	8	1207	2.16	158	183	1313
1140	4	1154	1.90	146	192	1349
1140	8	1226	2.25	163	189	1336
1170	4	1172	1.99	150	198	1374
1170	8	1246	2.36	168	195	1361

[a] Vibrational energy of 1,3-cyclohexadiene at the coupled temperature and at its nascent vibrational temperature.

Table III. The Vibrational Temperature and Energy of CO after Energy Transfer[a]

$T(T_r)$, K	T_{vCO}, K	E_{vCO} (T_{vC}), kJ mol^{-1}	E_{vBDE} (T_{vC}), kJ mol^{-1}	E_{vBDE} (T_{vBDE_i}), kJ mol^{-1}	T_{vBDE_i}, K
1330	1235	2.30	108	135	1405
1360	1246	2.36	110	137	1420
1390	1255	2.40	111	139	1431
1420	1258	2.42	112	139	1435
1450	1265	2.46	113	141	1445
1480	1271	2.49	114	142	1452

[a] Vibrational energy of butadiene at the coupled temperature and its nascent vibrational temperature from an 8% 3-cyclopentenone in CO mixture.

3-Cyclopentenone. The investigation of the thermal dissociation of 3-cyclopentenone followed a similar course to that of norbornenone. In our earlier study we determined the rate constants for the thermal dissociation of this molecule in Ar and showed that the CO is born with less than its statistical share of the energy released from the transition state.[7]

We measured the rate constant for its dissociation in CO at 1130 K and found the value close to that in Ar.

In separate experiments, we measured rate constants for the vibrational relaxation of CO by butadiene. These are given in Table I.

From the laser absorption experiments between 1320 and 1480 K we determined the vibrational temperature of the CO after energy transfer from the butadiene produced. The results were treated in a similar way to those with norbornenone to derive the nascent conditions of the butadiene. The results are given in Table III.

Discussion

The assignment of energy to internal vibration of the organic product and to translation, based on the measurement of the vibrational energy in the CO and the assumption of a statistical distribution,[11] is bound to be subject to very considerable uncertainty since, for a statistical distribution, only a very small fraction of the vibrational energy is partitioned into the CO. For the dissociation of norbornenone into 1,3-cyclohexadiene and CO, if there is a statistical distribution of vibrational energy, >95% of this energy goes into the 1,3-cyclohexadiene, which has 36 fundamental vibrations, 28 of which are of lower frequency than CO.[22] The distribution is also strongly weighted to butadiene, which has 24 normal modes.[33]

Provided that there is rapid (VV) transfer between the vibrationally excited organic product and CO, it is much more satisfactory to run the dissociation experiment with 4% or 8% of the organic molecule in CO. This gives about 28% of the vibrational energy in the CO for a 4% mixture of norbornenone and 16% for an 8% mixture; with 8% of 3-cyclopentenone about 25% of the vibrational energy will partition into the CO.

The major difference between using CO to monitor the vibrational state of N_2 in its relaxation by He and using CO to monitor the vibrational energy in these organic molecules is that in the former case there is a very large difference in the rate constants for (VV) coupling and (VT) deactivation and in the latter this difference is much smaller. This is to be expected since both 1,3-cyclohexadiene[22] and butadiene[33] have low-frequency fundamental vibrations, giving large rate constants for their (VT) relaxation and no fundamental vibrations close to the frequency of CO to ensure very fast (VV) coupling. At equilibrium translational temperatures of about 1250 K there are very small populations in the higher vibrational levels in CO and hence vibrational relaxation causes the upper state populations to cascade down to the equilibrium condition. These processes occur on the slower time scale than the excitation as can be seen in Figures 1 and 2.

For these reasons, even if the organic products are born with little vibrational energy, they will acquire this by process 10 and transfer it to CO by process 11. This will lead to the production of vibrationally excited CO, with the distribution appropriate to the translational temperature. It is the production of distributions removed from the equilibrium condition and their subsequent relaxation to equilibrium which proves that the organic products are excited initially with vibrational energies above the equilibrium values.

It is interesting to compare the nascent vibrational energies in 1,3-cyclohexadiene calculated from these results with the energy available for partitioning.

The heat of formation of norbornenone can be estimated from those of norbornanone, −134.1 ± 3.1 kJ mol^{-1},[34] norbornane, −54.9 ± 4.7 kJ mol^{-1},[34] and norbornene, 90 ± 3.2 kJ mol^{-1}.[34]

(12)

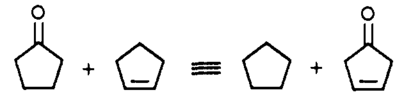
On the assumption that the strain energy in norbornanone is the same as in norbornane and that in norbornenone is the same as that in norbornene, the heat of formation of norbornenone is 10.8 kJ mol^{-1}.

The heat of formation of CO is −110.53 ± 0.17 kJ mol^{-1} at 298 K[35] and that of gaseous 1,3-cyclohexadiene[34] 106.2 ± 0.9 kJ mol^{-1}. These values lead to the enthalpy change on dissociation being −15 kJ mol^{-1}. The uncertainty in this value must be at least ±10 kJ mol^{-1}. Taking the activation energy as 146 ± 6 kJ mol^{-1}[7] gives the available energy as 161 ± 20 kJ mol^{-1} plus the energy in the transition state.

The results in Table II show that a large fraction of the available energy goes into the vibration of the 1,3-cyclohexadiene.

These experiments have shown that in the transition state the CO must have relaxed to a length close to that in the free molecule, but they are unable to show whether the bonds stretch synchronously and symmetrically or whether dissociation occurs via very asymmetric bond cleavage or via a diradical. Further insight into the mechanism would be gained from measurements of the nascent translational and rotational energies of the CO.

The same picture emerges for the thermal dissociation of 3-cyclopentenone.



(13)

The heat of formation of 3-cyclopentenone can be estimated from those of cyclopentanone, cyclopentane, and cyclopentene, since no conjugated system is introduced and the strain energies in cyclopentanone and cyclopentane are likely to be close, as are those of 3-cyclopentenone and cyclopentene. The heat of formation of cyclopentanone is −192.1 ± 1.8 kJ mol^{-1},[34] that of cyclopentane −76.4 ± 0.8 kJ mol^{-1},[34] and that of cyclopentene 33.9 ± 1.4 kJ mol^{-1}.[34] This leads to the value of −81.8 kJ mol^{-1} for the heat of formation of 3-cyclopentenone.

The heat of formation of CO at 298 K is −110.53 ± 0.17 kJ mol^{-1} and that of butadiene 110.0 ± 1.1 kJ mol^{-1}.[34] Hence the dissociation of 3-cyclopentenone is estimated to be endothermic by 82 ± 10 kJ mol^{-1}. The energy of activation has been measured by Dolbier and Frey[12] to be 214 ± 0.8 kJ mol^{-1}, giving the available energy as 132 ± 15 kJ mol^{-1} plus the energy in the transition state.

The results in Table III show that a large fraction of the available energy goes into the vibration of the butadiene.

The dissociation of these two molecules may be contrasted with those of the thermal dissociation of norbornanone and of 2-cyclopentenone in Ar. In both of these cases the CO is detected with the vibrational energy distribution appropriate to the translational temperature.[36] This raises the question as to what factor there is in the dynamics of the dissociations of norbornenone and 3-cyclopentenone, which gives rise to highly vibrationally excited organic products and less than the statistical share of the available energy in the vibration of the CO. These findings are similar to those of Dougherty et al. for the dissociation of **1**, who concluded that the major energy release is due to the rearrangement of the organic product, which occurs after the N_2 has become decoupled from the rest of the molecule.[8]

We suggest that the dissociation of these carbonyl compounds proceeds in a similar fashion, with the CO being decoupled from the rest of the molecule before the energy is released due to the rearrangement of the organic fragment. Direct evidence as to whether the CO dissociates by the symmetric or asymmetric cleavage of the two bonds from the CO group is given by experiments that show whether the CO molecule is born with a small or large amount of rotational energy. This evidence cannot be obtained from these thermal experiments since collisions that dissociate the molecule will cause very fast rotational relaxation. However, the nascent rotational distribution can be found from photochemical experiments with use of a tunable vacuum UV laser. These have been performed and show that the CO is born highly rotationally excited.[37] This proves that the photochemical dissociation does not occur by symmetrical bond cleavage.

---

(33) Shimanouchi, T. *National Bureau of Standards Tables of Molecular Vibrational Frequencies*; NSRDS-NBSJA; National Bureau of Standards: Washington, DC, 1972.

(34) Pedley, J. B.; Naylor, R. D.; Kirby, J. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(35) Chase, M. W., Jr.; Davies, L. A.; Downey, J. R., Jr.; Frurip, D. J.; McCondald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; National Bureau of Standards, Washington, DC, 1985; Part I.

(36) Wood, G. R.; Alston, K.; Simpson, C. J. S. M. To be published.

(37) Kable, S. H.; Houston, P. L.; Simpson, C. J. S. M. *J. Am. Chem. Soc.* To be published.