exclusively for complexes with one molecule. Charge-transfer electronic absorption may still occur within larger complexes, but it cannot be followed by these experiments because dissociation is not observed.

This work also represents the first photochemistry study on cluster–organic complexes containing more than two metal atoms. Even at this modest size, it is apparent that the information gained from such studies may be limited because of the numerous structural isomers possible. It is difficult to draw conclusions on photochemical mechanisms when the structures of the ions are not known. Tunable laser dissociation studies, following each product channel, may make it possible to achieve some separation of isomers in these studies. Another possibility is to modify the source to separate the growth region where metal condenses from the region where organic adsorbates are added. This procedure should eliminate the formation of sandwich structures. When these details can be worked out, experiments such as these may provide cluster analogues to photochemistry studies on bulk metal surfaces.[38,39]

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Dynamics of the Thermal Decomposition of 2,3-Diazabicyclo[2.2.1]hept-2-ene

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Abstract: The dynamics of the thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) have been investigated over the temperature range 900–1400 K. A tunable continuous wave CO laser was used to follow the vibrational energy content of the coupled CO–N_2 system from the initial to the equilibrium conditions. It has been shown that the N_2 is born with very little vibrational energy, while the bicyclo[2.1.0]pentane is born with an excess over the equilibrium distribution. These results provide clear evidence against the concerted decomposition mechanism.

Introduction

Thermal decomposition reactions cannot be investigated in the same detail as photochemical processes carried out under collision-free conditions, since the collisions necessary to cause the thermal relaxation also relax the initial energy states of the products. This applies to the nascent rotational states of thermolysis products in all carrier gases, because all molecules except hydrogen are very efficiently rotationally relaxed by all collision partners. However, this is not true of the vibrational relaxation of the diatomic molecules CO and N_2 by argon, which takes far longer than the observation times of these experiments.[1,2] This allows the possibility of determining the nascent vibrational state of CO formed from the thermal decomposition of carbonyl compounds and of N_2 produced from azo compounds.

We have investigated the thermal decomposition of carbonyl compounds, including 3-cyclopentenone and 7-norbornenone (bicyclo[2.2.1]hept-2-en-7-one) in argon.[3] We used a shock tube to obtain the desired temperature jump to a constant high temperature and measured the production of CO ($v = 0$) and CO ($v = 1$) using a continuous wave CO laser. The rate of production of CO ($v = 0$) enabled us to determine the rate constants for dissociation over the range of temperature from 1000 to 1350 K for 3-cyclopentenone and from 700 to 850 K for 7-norbornenone. In these temperature ranges, the rates of relaxation of the CO were governed by the collisions with the butadiene produced from the 3-cyclopentenone and the 1,3-cyclohexadiene produced from the 7-norbornenone. We determined the rate constants for these processes using mixtures of CO with butadiene in Ar and CO with 1,3-cyclohexadiene in Ar. We then chose mixture compositions such that the CO was relaxed to the final equilibrium condition before the end of the observation time of about 500 μs. We calculated these equilibrium conditions from the shock speeds and the Rankine–Hugeniot equations.[4] We observed the changes in the populations of CO ($v = 0$) and CO ($v = 1$) from when decomposition was complete to when the final equilibrium condition was reached. If the CO were born with an initial vibrational temperature, T_i, higher than the equilibrium temperature, then the population in $v = 1$ would fall on approaching equilibrium and that in $v = 0$ would rise. In fact, for both decompositions, the vibrational population in $v = 1$ increases and that in $v = 0$ decreases with time, showing that the CO is born vibrationally cold. Calculations revealed that the CO is born with less than its statistical share of the energy released. This is contrary to the suggestion of Bauer[5] that the CO might be born highly vibrationally excited, due to the contraction of the C–O bond length from that in the ketone to that of free CO.

In later experiments, we coupled the vibrational energy in the butadiene or 1,3-cyclohexadiene to CO and thus determined the nascent vibrational energies of these organic products. Both are born vibrationally excited.[6]

The bicyclic azoalkanes 2,3-diazabicyclo[2.1.1]hex-2-ene and DBH (2,3-diazabicyclo[2.2.1]hept-2-ene) would be expected to give nitrogen in a highly vibrationally excited state following synchronous rupture of the two C–N bonds, since the N–N axis would be orthogonal to the reaction coordinate.[5]

Dougherty and co-workers[7] deduced by a rather indirect means that the N_2 formed from 2,3-diazabicyclo[2.1.1]hex-2-ene does

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not have more than one vibrational quantum. They measured the yield of bicyclobutane and butadiene as a function of the pressure of added benzene, which collisionally deactivates vibrationally excited bicyclobutane. From a RRKM calculation, they estimated what energy the bicyclobutane must have to isomerize and give butadiene before it is deactivated. Since this energy is only a little less than the energy released on dissociation, they deduced that the energy available for the N_2 is less than one vibrational quantum. A possible weakness in this argument is that they did not know the energy in the initial transition state.

Recently Adams et al.[8] have used transient CARS spectroscopy to investigate the photochemical decomposition of DBH. They found the N_2 to be born with 84% in $v = 0$ and 12% in $v = 1$. They concluded that the photochemical decomposition occurs via a stepwise mechanism.

In our thermal decomposition experiments, we cannot directly monitor the nascent vibrational state of the N_2 produced, because we do not have transient CARS spectroscopy attached to our shock tube. However, if we select conditions such that the N_2^* is vibrationally coupled to CO, then we can measure the vibrational state of the CO and infer that of the N_2.

We worked with mixtures of DBH and CO in argon at temperatures between 900 and 1400 K, with post shock pressures between 50 and 200 Torr. The argon ensures that the DBH is dissociated in less than 1 μs under nearly isothermal conditions. The bicyclo[2.1.0]pentane (housane) produced may subsequently isomerize to cyclopentene,[9] but this will not affect the vibrational state of the N_2 formed. The argon will relax the housane or cyclopentene very rapidly to the equilibrium temperature. However, neither the argon nor the CO will vibrationally relax the N_2^* on the time scale of these experiments.[2,10]

Two processes excite the CO from its vibrational temperature of 300 K directly after the shock to the equilibrium temperature of 900–1400 K. The first is vibrational coupling with N_2^*, eq 1. This will be followed by (VV) coupling, giving a vibrational

$$\mathrm{N_2}\ (v = m) + \mathrm{CO}\ (v = 0) \rightleftharpoons \mathrm{N_2}\ (v = m - 1) + \mathrm{CO}\ (v = 1) \qquad (1)$$

temperature to the system by processes such as that in eq 2. The

$$\mathrm{CO}\ (v = n) + \mathrm{CO}\ (v = 1) \rightleftharpoons \mathrm{CO}\ (v = n + 1) + \mathrm{CO}\ (v = 0) \qquad (2)$$

second process is collisional activation by the housane or cyclopentene, eq 3. This will drive the CO to vibrational equilibration with the translational temperature.

$$\mathrm{CO} + \mathrm{M} \rightarrow \mathrm{CO}^* + \mathrm{M} \qquad (3)$$

We need to make processes 1 and 2 faster than process 3 so that we are considering a vibrational system that is not coupled to the translational temperature. This situation will be favored by a high ratio of CO to DBH. However, the higher this ratio, then the smaller will be the effect of the N_2^* in producing vibrationally excited CO.

The rate constants for process 1 are known as a function of temperature.[10] Our first task was to determine rate constants for the vibrational excitation of CO by cyclopentene in the temperature range 900–1400 K. With these data, we calculated that, using a mixture with 1% DBH, 10% CO, and 89% Ar, the times for the coupling reactions 1 and 2 will be about one-third to one-quarter of those to relax CO by process 3.

If the N_2^* is produced highly vibrationally excited, then the CO will be driven to a vibrational temperature higher than the equilibrium temperature and will subsequently relax to the equilibrium condition. The vibrational population in the CO will rise to a maximum and then fall to the equilibrium condition. This will be more easily seen the lower the equilibrium temperature. This is the reason we worked down to 900 K, where the CO has only 3.1% of its population in $v = 1$.

If the N_2 has just enough vibrational energy to drive the CO to the equilibrium translational temperature, then equilibrium will be reached in a shorter time than that due to process 3.

If the N_2 is born with very little vibrational energy, then the relaxation will be dominated by process 3. In this case, the CO laser gain against time curve will closely resemble that for the relaxation of CO by cyclopentene in Ar under the same conditions as for the DBH, CO, and Ar mixture.

The cyclopentene, CO, and Ar gain versus time curves give a measure of the changing vibrational temperature of the CO from 300 K to the equilibrium temperature. If the N_2 is born vibrationally cold, then the comparison of the gain–time curves of cyclopentene and DBH mixtures, at times before equilibrium is reached, but after processes 1 and 2 are complete, will be a sensitive method of determining the vibrational energy content of the N_2.

Experimental Section

The shock tube has many advantages for studying thermal decomposition reactions. These include homogeneous heating, that any desired temperature between 400 and 3000 K may be selected, and that following the temperature jump the conditions are nearly uniform for 500 μs in the absence of any reaction. The magnitude of the temperature jump depends upon the ratio of the pressures of the driver and test gases and not on their absolute pressures. Consequently, test gas pressures may be chosen to ensure that energy transfer processes are complete within the 500-μs time scale. The vibrational distribution in CO produced by reactions can be measured by using a line tunable continuous wave CO laser set to traverse the shock tube. The time resolution is controlled by the transit time of the shock-heated gas across the laser beam and is about 1 μs. This system is well suited for measuring the rates of reactions producing CO and of energy transfer processes involving CO.

In this study, we monitored the vibrational state of the CO by measuring the change in intensity of the CO ($v = 3 \rightarrow 2$) P(10) line at the far side of the shock tube. The gain is defined by eq 4, in which I_0

$$G\ (3 \rightarrow 2) = \ln \left[\frac{I_0 - \Delta I}{I_0} \right] \qquad (4)$$

is the incident laser intensity. The gain depends upon the difference between absorption and stimulated emission. For the $v = 3 \rightarrow 2$ P(10) line, this may be expressed by eq 5.

$$G\ (3 \rightarrow 2) = {}^1\!/_{19} n_{v=3,J=9} - {}^1\!/_{21} n_{v=2,J=10} \qquad (5)$$

The DBH was synthesized by the method of Gassman and Mansfield.[11]

Results

In our investigations of the vibrational energy distribution following thermolysis of the ketones 3-cyclopentenone and 7-norbornenone,[3,6] we first worked with mixtures containing a few percent of the keto compound in Ar, and then with a few percent of the keto compound in CO. In the Ar mixtures under the conditions used, the dissociation takes place in less than 5 μs, yielding CO and butadiene and CO and 1,3-cyclohexadiene, respectively. The vibrational deactivation of the butadiene and the 1,3-cyclohexadiene by the Ar takes place in under 10 μs.[12]

$$\mathrm{M}^{**} + \mathrm{Ar} \rightarrow \mathrm{M}^* + \mathrm{Ar} \qquad (6)$$

M^{**} represents the initially vibrationally excited molecule and M^* the molecule relaxed to the translational temperature.

The rate constants for the vibrational relaxation of both vibrationally excited and ground-state CO by Ar are too small for appreciable relaxation to occur in the observation times of about 500 μs.[1]

$$\mathrm{CO} + \mathrm{Ar} \rightarrow \mathrm{CO}^* + \mathrm{Ar} \qquad (7)$$

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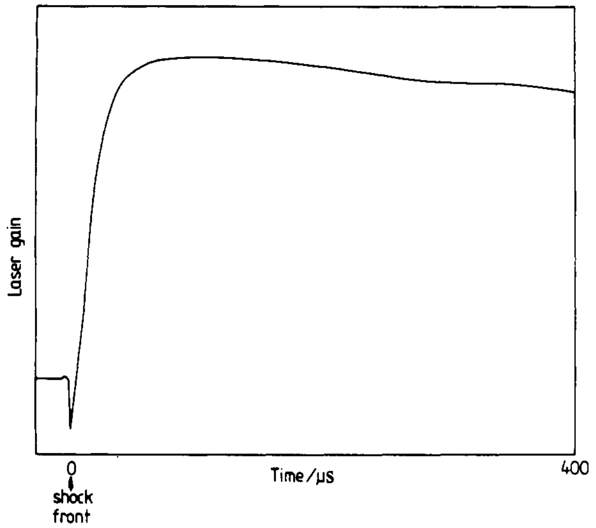

Figure 1. Laser gain curve for ($v = 3 \rightarrow 2$) P(10) for 1% DBH in CO (p = 215 Torr, T = 1607 K, time scale = 400 μs across trace).

The species responsible for relaxing the CO to the equilibrium temperature are the butadiene and the 1,3-cyclohexadiene. Since we had measured the rate constants for these processes, we were able to choose conditions such that the relaxation of the CO took place in about 200 μs. If the CO were born with a vibrational temperature greater than the translational temperature, then its vibrational population would be decreased to the equilibrium value by means of processes 8 and 9. If the CO were born with less

$$CO^{**} + M \rightarrow CO^{*} + M^{**} \quad (8)$$

$$M^{**} + Ar \rightarrow M^{*} + Ar \quad (9)$$

than the equilibrium vibrational energy content, then it would be excited to this value by processes 10 and 11. Since we can easily calculate the amount of CO* from the known translational temperature, it is immediately apparent whether the CO is born with more or less vibrational energy than it possesses at equilibrium, by whether relaxation takes place down to or up to the equilibrium value of T_e.

$$CO + M \rightarrow CO^{*} + M \quad (10)$$

$$M + Ar \rightarrow M^{*} + Ar \quad (11)$$

When we had established that, in both of these cases, the CO is born with less than the equilibrium value at T_e, we dissociated both molecules with CO as carrier gas. In this instance, energy transfer from M** to CO occurs at a greater rate than deactivation of these molecules by unexcited CO. Process 12 is faster than process 13.

$$M^{**} + CO \rightleftharpoons M^{*} + CO^{*} \quad (12)$$

$$M^{**} + CO \rightarrow M^{*} + CO \quad (13)$$

Using this technique, we showed that the butadiene and the 1,3-cyclohexadiene were both born with more than the equilibrium content of vibrational energy.

It is a more difficult problem to allocate the nascent vibrational energy distribution between housane (or cyclopentene) and N_2 following thermal decomposition of DBH. We first used from 4 to 1% of DBH in CO dissociated over the temperature range 1300–1500 K. We found that the vibrational energy content of the CO rises to a maximum and then falls to its equilibrium value. This is shown in Figure 1. Under these conditions, the rates of energy transfer from N_2^{**} and M** to CO are both high and we cannot tell whether the production of an excess of vibrational energy in CO is due to N_2^{**}, M**, or both molecules.

We measured the rate constants for the vibrational relaxation of CO by cyclopentene in the temperature range 900–1400 K. The results are shown in Table I and Figure 2. The times for the relaxation of CO** to CO* following dissociation of DBH are consistent with this being due to housane or cyclopentene.

Table I. Gains and Rate Constants for Cyclopentene

T (K)	$-G_{max}/p_{CO}$ (Torr^{-1})	k (cm^3 molecule^{-1} s^{-1})
944	2.55×10^{-3}	5.17×10^{-13}
969	4.35×10^{-3}	4.50×10^{-13}
1020	6.48×10^{-3}	5.87×10^{-13}
1043	5.46×10^{-3}	6.23×10^{-13}
1068	8.38×10^{-3}	5.42×10^{-13}
1100	6.27×10^{-3}	5.83×10^{-13}
1119	9.29×10^{-3}	5.65×10^{-13}
1127	1.01×10^{-2}	6.92×10^{-13}
1154	1.21×10^{-2}	6.47×10^{-13}
1190	1.13×10^{-2}	8.68×10^{-13}
1294	1.76×10^{-2}	1.04×10^{-12}
1357	1.70×10^{-2}	1.54×10^{-12}

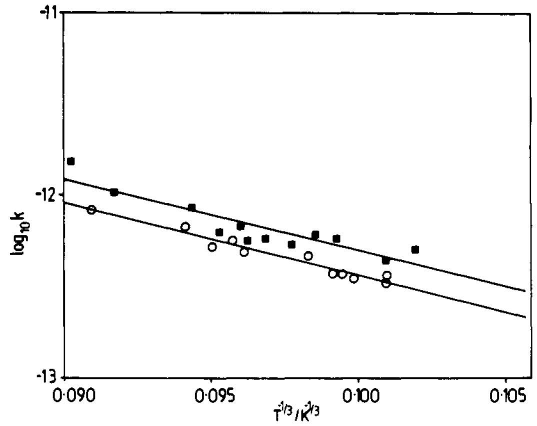

Figure 2. Rate constants for the production of vibrationally excited CO monitored with ($v = 3 \rightarrow 2$) P(10) for ■, 1% cyclopentene, 10% CO, and 89% Ar; and ○, 1% DBH, 10% CO, and 89% Ar.

We then carried out a series of experiments using DBH, CO, and Ar mixtures, gradually decreasing the percentage of CO and increasing that of Ar. As this change in composition is made, the rate of the coupling process 14 falls and that of the deactivation process 15, where X is CO or Ar, rises.

$$M^{**} + CO \rightleftharpoons M^{*} + CO^{**} \quad (14)$$

$$M^{**} + X \rightarrow M^{*} + X \quad (15)$$

Under these experimental conditions, the rate of deactivation of vibrationally excited N_2^{**} by CO or Ar is negligible. The rate of energy transfer from N_2^{**} to CO falls, due to the reduced number density of CO. For the post shock pressures and temperatures used, energy transfer from N_2^{**} to CO is complete in 50–90 μs for mixtures containing 1% DBH, 10% CO, and 89% Ar. Since the CO and Ar are expected to have comparable rate constants for deactivating vibrationally excited housane or cyclopentene, the rate of deactivation of these molecules relative to that of energy transfer has risen by a factor of 10; these organic molecules are then deactivated in a few microseconds.

In the temperature range 900–1400 K with post shock pressures of 50–200 Torr, we have calculated that the cyclopentene will relax the CO within the observation time, using the rate constants given in Table I. During this process, the CO will relax through a series of Boltzmann distributions brought about by (VV) processes such as 16. If the contribution of process 17 to the vibrational ex-

$$CO\ (v = 1) + CO\ (v = 1) \rightleftharpoons CO\ (v = 2) + CO\ (v = 0) \quad (16)$$

citation of the CO is negligible compared to those of processes 18 and 19, then the rates of production of CO* from 1% DBH, 10% CO, and 89% Ar mixtures will be very similar to those for the mixture 1% cyclopentene, 10% CO, and 89% Ar under the same experimental conditions. However, if the N_2^{**} makes a

$$N_2^{**} + CO \rightleftharpoons N_2^{*} + CO^{*} \quad (17)$$

large contribution to the excitation of CO, then there will be

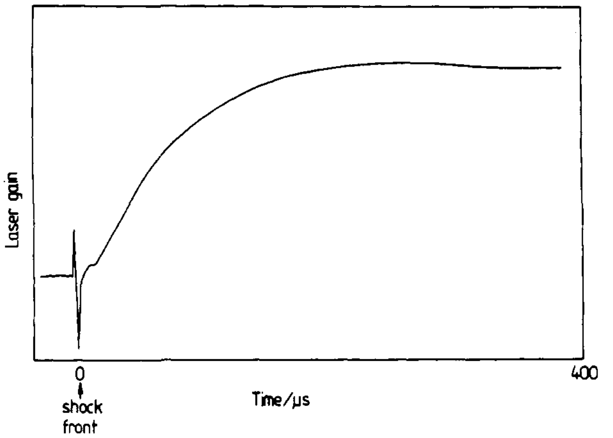

Figure 3. Laser gain curve for ($v = 3 \rightarrow 2$) P(10) for 1% cyclopentene, 10% CO, and 89% Ar (p = 58 Torr, T = 1357 K, time scale = 400 µs across trace).

Table II. Gains and Rate Constants for DBH

T (K)	$-G/p_{CO}$ (Torr^{-1})	k (cm^3 molecule^{-1} s^{-1})
973	3.96×10^{-3}	3.33×10^{-13}
978	6.15×10^{-3}	3.64×10^{-13}
1002	6.02×10^{-3}	3.51×10^{-13}
1015	6.52×10^{-3}	3.73×10^{-13}
1025	6.12×10^{-3}	3.76×10^{-13}
1049	7.29×10^{-3}	4.73×10^{-13}
1122	1.02×10^{-2}	4.94×10^{-13}
1139	1.33×10^{-2}	5.64×10^{-13}
1161	1.12×10^{-2}	5.26×10^{-13}
1196	1.16×10^{-2}	6.77×10^{-13}
1325	1.82×10^{-2}	8.44×10^{-13}

production of CO** above the equilibrium value of CO* by about 90 µs, followed by relaxation to CO* by about 400 µs. If the N_2** makes a smaller but substantial contribution, then the production of CO* will occur by 90 µs rather than by 400 µs.

$$CO + M^* \rightarrow CO^* + M \qquad (18)$$

$$M + Ar \rightarrow M^* + Ar \qquad (19)$$

The rate constants for the production of CO* by cyclopentene at the values of T_e are given in Table I for the temperature range 900–1400 K. A typical result for the change in laser absorption for the 1% cyclopentene, 10% CO, and 89% Ar mixtures is shown in Figure 3.

In Table II, results are presented for the 1% DBH, 10% CO, and 89% Ar mixtures carried out for the same ranges of post shock temperatures and pressures. A typical laser absorption trace is shown in Figure 4. The laser absorption traces for these two mixtures taken under the same conditions appear identical, showing immediately that there can be no major production of N_2**. The laser gains measured once equilibrium has been reached for the cyclopentene mixtures serve to calibrate laser gain against CO vibrational temperature. The results are plotted in Figure 5. Also plotted on this figure are the laser gains at equilibrium for the DBH mixtures. These results fall on the same line showing that the DBH mixtures have relaxed to the same CO vibrational temperature at equilibrium.

That the CO is relaxed at the same rate in these two mixtures is established from a comparison of the laser gains at one-third of the time to equilibration. At this time, energy transfer from N_2** would be complete. The percentages in CO ($v = 1$) at this time are 1.2% for the equilibrium temperature of 950 K and 1.9% for the equilibrium temperature of 1100 K. If all this excitation in the CO were due to N_2**, then the N_2** would possess 0.1 quantum of vibrational excitation for dissociation at 950 K, and 0.2 quantum at 1100 K. However, the comparison between the laser gain curves of cyclopentene and DBH mixtures shows that at least 50% of this excitation must be due to relaxation of the CO by the organic product. This sets the maximum excitation in the N_2** between 5 ± 3% in $v = 1$ at 950 K and 10 ± 5% in $v = 1$ at 1100 K.

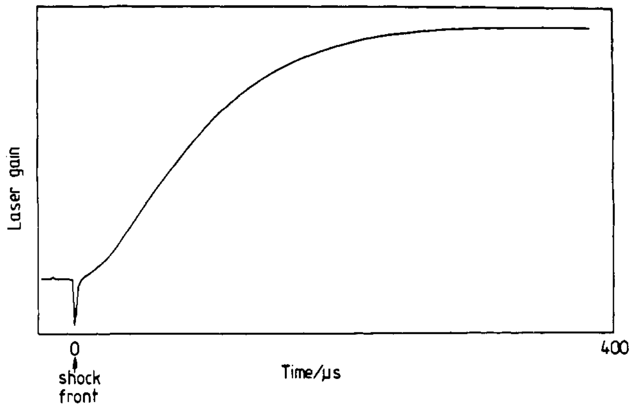

Figure 4. Laser gain curve for ($v = 3 \rightarrow 2$) P(10) for 1% DBH, 10% CO, and 89% Ar (p = 58 Torr, T = 1325 K, time scale = 400 µs across trace).

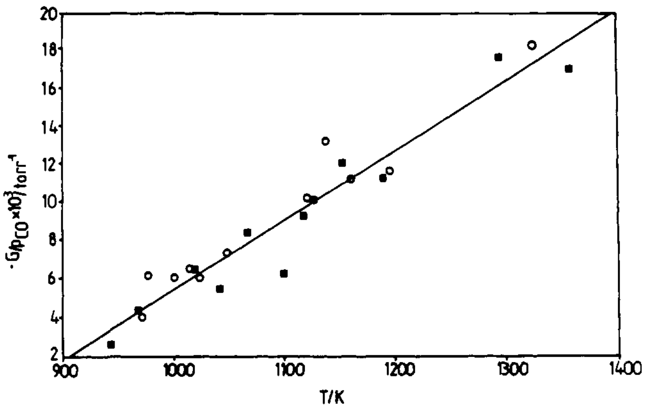

Figure 5. Variation with temperature of laser gain/pressure: ($v = 3 \rightarrow 2$) P(10) for ■, 1% cyclopentene, 10% CO, and 89% Ar; and ○, 1% DBH, 10% CO, and 89% Ar. Results plotted as $-G_{max}/p_{CO} \times 10^3$ (Torr^{-1}) against T (K).

An alternative approach is to plot the rate constants for the vibrational relaxation of the CO in these two mixtures against the translational temperature. This data is given in Figure 2. The small differences found are only just greater than the experimental errors. They either reflect small differences in the rate constants for relaxation of CO by housane and cyclopentene or small contributions from N_2**. If we assume that the difference is due to the presence of N_2**, we again conclude that there are maximum values of 5 ± 3% in $v = 1$ at 950 K and 10 ± 5% at 1100 K.

Discussion

The original postulate of Bauer[5] was that synchronous bond cleavage would lead to highly vibrationally excited N_2. This is because the N=N group is orthogonal to the reaction coordinate and there is a large change in bond length between the N=N group in DBH at 1.246 Å[13] and that of free nitrogen at 1.098 Å.[14] Our experiments clearly show that the N_2 is not born with large amounts of vibrational energy. This establishes that there must be stepwise dissociation, with the N=N group contracting to a length close to that in free nitrogen before rupture of the second C—N=N bond.

Now that we have shown that there is little nascent vibrational energy in the N_2**, our results for the thermal dissociation of DBH in pure CO show that the housane is born vibrationally excited. This supports the hypothesis that the major energy release of the reaction occurs after the N_2 group has become decoupled from the rest of the molecule.

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It is interesting that these findings for the thermal decomposition of DBH are very similar to those obtained by Adams et al.[8] for the photochemical dissociation. The conditions necessary for the collisional thermal decomposition preclude the possibility of analysis of the rotational state of nascent nitrogen. This is unfortunate, since it would be interesting to know whether the N_2 is born rotationally cold, as found by Adams el al. for the photolysis of DBH. The small degree of rotational excitation in the N_2 is unexpected and is in great contrast to recent findings that CO is born with large amounts of rotational excitation in the photochemical dissociation of 3-cyclopentenone and 7-norbornenone.[15]

Registry No. DBH, 2721-32-6; CO, 630-08-0; cyclopentene, 142-29-0.

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Structure of the Trimethylamine–Sulfur Dioxide Complex

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Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055. Received October 19, 1990

Abstract: The microwave spectrum of the charge-transfer complex between trimethylamine and sulfur dioxide has been studied with a pulsed molecular beam Fourier transform microwave spectrometer. In addition to the normal isotopic form, the rotational spectra of the $(CH_3)_3N{\cdot}^{34}SO_2$, $(CH_3)_3{}^{15}N{\cdot}SO_2$, $(CH_3)_3N{\cdot}SO^{18}O$, $(CH_3)_3N{\cdot}S^{18}O_2$, and $^{13}CH_3(CH_3)_2N{\cdot}SO_2$ isotopic species were assigned. Stark effect measurements gave electric dipole components of $\mu_a = 4.676$ (5), $\mu_c = 1.081$ (4), and $\mu_{total} = 4.800$ (5) D. The dipole moment and moment of inertia data show that the complex belongs to the C_s point group. The crystal structure of the charge-transfer complex has been reexamined at −70 °C by X-ray crystallography and is in good agreement with an earlier room-temperature determination. The structure of this complex in both the gas and solid phase is consistent with the nitrogen lone pair pointing toward the sulfur atom, with the SO_2 plane tilted by ~75° from the C_3 axis of the trimethylamine. The methyl groups are staggered with respect to the oxygen atoms. In the gas phase, the nitrogen to sulfur distance is 2.26 (3) Å; this distance shortens to 2.05 (1) Å in the crystal. From the dipole moment and the nitrogen nuclear quadrupole coupling constants, an upper limit was estimated for the transfer of charge from the nitrogen to the sulfur atom as 0.2 to 0.3 electron.

Introduction

The trimethylamine–sulfur dioxide ($TMA{\cdot}SO_2$) complex is one of the most thoroughly studied amine·SO_2 charge-transfer complexes.[1] This 1:1 addition compound forms a readily sublimable white solid with a melting point of 77 °C.[2,3] The charge-transfer band of the complex occurs at 276 nm in the gas phase and shows an unusual blue shift upon solvation to 273 nm in heptane and 258 nm in dichloromethane.[4-6] From this absorption feature, as well as from pressure measurements, the reaction thermodynamics were evaluated in the gas phase and in heptane solvent.[5] The solvation energies for the free species and the lattice energy for the complex were also determined, allowing a complete thermodynamic cycle to be constructed. The dissociation energy was found to be 9.1 (4) kcal/mol in the gas phase and 11.0 (5) kcal/mol in heptane. The unusual blue shift and the increased stability upon solvation were explained by strong dipole-induced dipole interactions with the solvent which stabilize the ground state of the complex more than free TMA and SO_2. This was consistent with the large dipole moment of 4.95 (5) D determined for the complex in benzene.[3]

Table I. Previous Structural Studies of $(CH_3)_3N{\cdot}SO_2$

	ref				
	10	11	12, 13	7	17
method	STO-3G	4-31G	3-21G[d]	X-ray	MW
d(N–S), Å[a]	2.86	2.36	2.13	2.06 (1)	2.27 (3)
α, deg	0[b]	0[b]	0[b]	0	19 (5)
β, deg	90[b]	85[b]	81	68	91 (2)
$-\Delta E$, kcal/mol[c]	4.06	14.8[e]	11.3		

[a] See Figure 1 for parameter definitions. [b] Assumed. [c] $TMA(g) + SO_2(g) \rightarrow TMA{\cdot}SO_2(g)$, =9.1 kcal/mol, experimental value.[5] [d] d polarization functions on N and S. [e] At d(N–S) = 2.45 Å.

It was proposed from the dipole moment and spectral data that the nitrogen end of TMA points to the plane of the SO_2, as expected for a n(lp)–π^* interaction,[3,5] and this was confirmed when the crystal structure was reported.[7] The C_3 axis of the TMA was essentially colinear with the "N–S bond". The N–S distance was 2.062 (6) Å with a tilt angle of 68° between the SO_2 plane and the N–S axis. This N–S distance, compared to the sum of the van der Waals radii (3.35 Å) and that of the covalent radii (1.74 Å)[8] for nitrogen and sulfur, implied an appreciable interaction and raised questions about possible small structural deformations in each monomer. This question could not be answered definitively because of the uncertainties in the structure analysis although several parameters showed deviations from the monomers. More insight on the interaction was obtained from an IR study of the methyl-substituted amines in argon and nitrogen matrices.[9] A shift in the IR bands of the SO_2 subunit was observed for all the complexes. For the $TMA{\cdot}SO_2$ complex the antisymmetric stretching mode decreased from 1350 cm^{-1} for free SO_2 to 1270

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