isoelectronic with CO. However, other considerations suggest that the chemical behavior of BF might be quite different from that of CO or N_2. In particular, electronic structure calculations indicate[30] that individual molecular orbitals of BF are quite asymmetric so that the small overall dipole moment could be misleading.

Nevertheless, Table V presents a comparison of isoelectronic rate coefficient data. Data are not available for $N_2 + NO_2$ or Cl_2. Indeed, the isoelectronic comparison is completely inappropriate for $N_2 + Cl_2$ because N_2Cl is not a stable molecule. The entries in the table indicate reasonable isoelectronic trends for the O, O_2, and Cl_2 reactions. Thus, BF and CO + Cl_2 both have negligible activation energy barriers, although the CO + Cl_2 reaction might have an endothermicity to overcome. The available information[31] on this reaction actually refers to the inverse reaction. Data for O atom and O_2 molecule reactions show reasonable trends, with N_2 the least reactive and BF the most reactive with either reagent. It is also noteworthy that preexponential terms are approximately the same within each of these isoelectronic series. However, this isoelectronic trends picture works less well for NO_2, with BF + NO_2 perhaps surprisingly fast in comparison with CO + NO_2. As a "pseudo-halogen", however, NO_2 might be expected to experience a stronger attractive interaction upon approach of BF as opposed to CO, and this may account for the much different reactivities.

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Registry No. BF, 13768-60-0; O_2, 7782-44-7; O, 17778-80-2; NO_2, 10102-43-9; Cl, 7782-50-5.

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Comparative Pulsed CO_2 Laser Pyrolysis. The Decarbonylation Reaction of Propynal

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Comparative transversely excited atmospheric (TEA) CO_2 laser pyrolysis was applied to determine the activation energy of the reaction $HC\equiv C-CHO \rightarrow HC\equiv CH + CO$. By use of three reference reactions, namely the H_2 elimination of cyclopentene and the dehydrohalogenation of vinyl chloride and vinyl bromide, the activation energy was found to be $E_a = 68 \pm 2$ kcal/mol. This result is in good agreement with $E_a = 69.9$ kcal/mol obtained from a previous ab initio SCF CI calculation of propynal's reaction path. The suitability of the method of comparative IR laser pyrolysis to determine activation energies is contrasted with its limitations when applied to evaluate frequency factors.

Introduction

Propynal, $HC\equiv C-CHO$, has shown to be a very suitable intermediate size molecule to explore the microscopic decay path of an electronically excited polyatomic molecule.[1-7] At moderate excess vibrational energies in the S_1 $(n\pi^*)$ state, its chemical decay behavior implies the elimination reaction[8]

$$HC\equiv C-CHO \rightarrow CO + HC\equiv CH$$

Since the spectral and dynamic data indicated the S_1 and T_1 potential surfaces not to be dissociative,[5,7] it was inferred that the dissociation takes place on the potential surface of the electronic ground state. Motivated by this result, extensive ab initio calculations at the CI level were performed to map the S_0 surface and to examine the chemical decay channels of this "intermediate case" test molecule.[6,7] The lowest reaction path predicted by the calculations is decarbonylation via a concerted mechanism which involves the migration of the aldehyde H atom in the molecular plane. Taking into account the zero-point energies, the barrier height was calculated to be 69.9 kcal/mol.[7] Thus, excitation into the S_1 vibrational ground state at 74.8 kcal/mol followed by internal conversion should lead to the chemical decay of propynal. This prediction has recently been confirmed by time-resolved experiments in which strong IR emission of nascent $CO(v=1)$ molecules was observed when the UV laser was turned to the 0_0^0 absorption band.[9] Based on this finding, an upper limit for the reaction barrier of 72 kcal/mol was estimated.[9]

In the present communication we report on comparative CO_2 laser pyrolyses of propynal. In order to determine the energy barrier of the lowest dissociation channel, sensitized IR laser heating was applied. In conjunction with the reference reactions $H_2C{=}CHCl \rightarrow HC\equiv CH + HCl$, $H_2C{=}CHBr \rightarrow HC\equiv CH + HBr$, and cyclopentene $\rightarrow$ cyclopentadiene + H_2, an activation energy of 68 ± 2 kcal/mol was found.

Experimental Section

In a first series of experiments propynal ($p = 1$ torr) was excited into its C–C stretching mode absorption ($\tilde{\nu}_6 = 944\ \mathrm{cm}^{-1}$ [10]) by TEA

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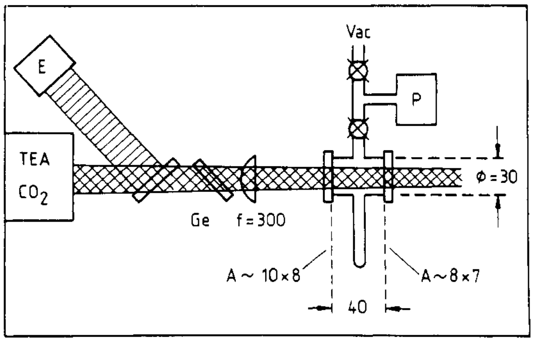

Figure 1. Experimental setup for TEA CO_2 laser pyrolysis. The laser beam is slightly focused by a NaCl lens. The cell, equipped with a side arm for liquid N_2 cooling, is connected to a vacuum line with a pressure head (P). A small portion of the laser beam is deflected onto an energy meter (E). Attenuation of the laser beam is achieved with a Ge flat. (The dimensions are given in millimeters.)

CO_2 laser irradiation at 944 cm^{-1} (P(20) line, 00^01–10^00 transition).[11] With a CO_2 laser energy flux $\Phi \leq 2$ J/cm^2 (23-mm beam diameter) the average energy deposited per molecule was found to be $\bar{E}_{abs} \leq 6600$ cm^{-1} when the previously determined cross section σ (p = 1 torr) of propynal was used.[3] Under these excitation conditions the chemical conversion per laser pulse was ≤1.8% of the irradiated molecules in the reaction cell of 600-mm length and 48-mm i.d. The products were quantitatively analyzed by monitoring the pressure and by gas chromatography. On the basis of earlier findings,[8] CO was regarded as the only volatile compound in the reaction mixture at 77 K. Its pressure $p_{CO} = p(77\ K)$ was measured by utilizing a capacitance manometer (MKS Baratron, 310-BHS-10 pressure head). On the other hand, the C_2H_2 yield was derived from the pressure ratio C_2H_2:propynal which was determined by a gas chromatograph (Carlo Erba, Fractovap Linea GI 450) equipped with a glass capillary (UCON LB 550X, 0.32-mm diameter, 50-m length, Jaeggi, Switzerland) and a flame ionization detector (FID). The experimental data thus obtained were the pressure ratios $p_{CO}{:}p_{C_2H_2} = 1.05 \pm 0.06$ and $(p_{initial} + p_{CO}){:}(p_{initial} + p_{C_2H_2}){:}p_{final} = (1.01 \pm 0.01){:}(1.02 \pm 0.1){:}1$. This result clearly demonstrates that TEA CO_2 laser excitation leads to a clean decarbonylation reaction $HC{\equiv}C{-}CHO \rightarrow HC{\equiv}CH + CO$.

Four series of experiments have been performed applying the method of comparative TEA CO_2 laser pyrolysis.[12] Figure 1 shows the experimental setup with a CO_2 laser Lumonics TE-260 ($\tilde{\nu}_L$ = 944 cm^{-1}). Homogeneous energy deposition in the reaction cell was achieved by slightly focusing the laser beam in order to roughly compensate for attenuation due to the probe absorption. The components of the reaction mixture were condensed into the liquid N_2 cooled side arm of the cell and then degassed and evaporated into the cell. In each experiment the reaction mixture consisted of a pair of educt compounds (typically 1 torr each), SF_6 sensitizer (5 torr), and Xe buffer gas (0–25 torr).

The following educt pairs (probe/reference) were investigated: propynal/vinyl chloride, propynal/vinyl bromide, propynal/cyclopentene, and vinyl bromide/cyclopentene. Vinyl chloride (Fluka, puriss.), vinyl bromide (Aldrich, 98% purity), cyclopentene (Fluka, puriss.), SF_6 (Matheson, 99.9% purity), and Xe (Linde Gas, 99.990% purity) were used as received. Propynal was synthesized according to a published procedure[13] and purified by gas chromatography.

The comparative pyrolysis experiments were performed at a pulse repetition frequency of 0.5 Hz to about 10% chemical conversion. This conversion was obtained with 5–4000 laser shots depending on the laser pulse energy. The reaction mixture was trapped at 77 K in the side arm of the cell. From the remaining vapor pressure (50–200 mtorr) the Xe equilibrium pressure at 77 K (~2 mtorr) was subtracted and the CO contribution of propynal, or the H_2 production from cyclopentene, or the sum of both gases determined. Furthermore, GC analysis yielded the pressure ratio between C_2H_2 and the unreacted educt which allowed the absolute amount of C_2H_2 to be determined. In case of the reaction pairs propynal/vinyl chloride and propynal/vinyl bromide the amount of C_2H_2 resulted from both educt decompositions. Since the C_2H_2 quantity originating from propynal is equimolar to that of CO (see above) and was thus readily determined, the remainder of C_2H_2 was obviously due to the vinyl halide decomposition. In the experiment with the propynal/cyclopentene pair the pressure at 77 K is the sum of the CO and H_2 pressures. In this case the equimolar production of CO and C_2H_2 from propynal was utilized to determine the CO contribution in the CO/H_2 mixture. Cyclopentene and its decomposition product cyclopentadiene could not properly be separated on the GC column. However, the composite peak area was found proportional to the sum of both compound concentrations owing to the same FID sensitivities of cyclopentene and cyclopentadiene.

Results

Pyrolysis experiments performed at laser pulse repetition frequencies not exceeding 0.5 Hz gave identical results indicating complete gas mixing in the reaction cell between the laser pulses. The conversion of the educt j into the product i after one laser pulse may be expressed in terms of the fraction of unreacted educts M_j^*/M_{j0}^* in the irradiated volume V_{irr}. Experimentally this ratio is obtained from the measured product yield Q_i after N laser pulses via the relationship

$$M_j^*/M_{j0}^* = 1 - \left\{1 - \left(\frac{M_{j0} - Q_i}{M_{j0}}\right)^{1/N}\right\}\frac{V_{cell}}{V_{irr}} \qquad (1)$$

where M_{j0} denotes the initial amount of educt in the cell volume V_{cell} (V_{cell}/V_{irr} = 16). The value of M_j^*/M_{j0}^* enters the model of comparative pyrolysis which was originally developed for single-pulse shock tube experiments[14] and later extended to sensitized TEA CO_2 laser decomposition.[12,15] The method compares the behavior of a suitable and well-known reference reaction with that of the reaction of interest. Briefly, the kinetic parameters of two independent, first-order reactions which follow an Arrhenius behavior over a common reaction time τ at a common temperature T are related by

$$\ln (k_1\tau) = \frac{E_1}{E_2} \ln (k_2\tau) + \ln A_1 - \frac{E_1}{E_2} \ln A_2 + \left(1 - \frac{E_1}{E_2}\right) \ln \tau \qquad (2)$$

where E is the activation energy and A the frequency factor. The reaction temperature T, usually not known in CO_2 laser experiments, is no longer contained in this equation. The variables ln $(k_1\tau)$ and ln $(k_2\tau)$ are then replaced by the ratio M_j^*/M_{j0}^* according to the expression

$$k_j\tau = -\ln (M_j^*/M_{j0}^*) \qquad (3)$$

With eq 2 and 3 the ratio of the unknown to the known activation energy is then given by

$$\frac{E_1}{E_2} = \frac{d \ln (k_1\tau)}{d \ln (k_2\tau)} = \frac{d \ln [-\ln (M_1^*/M_{10}^*)]}{d \ln [-\ln (M_2^*/M_{20}^*)]} \qquad (4)$$

and can be determined from the chemical conversion yield of a comparative pyrolysis experiment using various reaction tem-

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TABLE I: Partial and Total Pressures of the Reaction Mixture, Results of the Comparative Pyrolysis Experiments, Arrhenius Parameters of the Reference Reaction (E_{ref}, A_{ref}), Activation Energy, and Frequency Factor of the Probe Reaction (E_{pr}, A_{pr}) with Their Error Limits Obtained from the Experimental Results and the Reference Values

						results from Figure 2						ΔE_{pr}		
ref	p_{ref}, torr	probe	p_{pr}, torr	p_{Xe}, torr	p,[a] torr	symbols	slope[b]	intercept[b]	E_{ref}, kcal/mol	log A_{ref}/s^{-1}	E_{pr}, kcal/mol	slope	ref	log A_{pr}/s^{-1} [c]
cyclopentene	1	HCCCHO	1		7	circle	1.10 ± 0.04	−0.55 ± 0.15	61.0 ± 1.0[d]	13.35[d]	67.1	±2.4	±1.1	13.9 ± 0.25
				13	20	triangle								
				33	40	square								
H_2CCHCl	2	HCCCHO	1	12	20	square	1.01 ± 0.02	1.5 ± 0.15	69.3 ± 2.9[e]	14.0 ± 0.2[e]	69.7	±1.4	±2.9	14.8 ± 0.2
				17	25	circle								
				17	25	triangle								
H_2CCHBr	1	HCCCHO	1	13	20	square	1.04 ± 0.03	2.0 ± 0.2	64.9 ± 2.4[f]	13.3 ± 0.3[f]	67.7	±1.3	±2.4	14.4 ± 0.35
cyclopentene	1	H_2CCHBr	1	13	20	circle	0.94 ± 0.03	1.05 ± 0.15	61.0 ± 1.0[d]	13.35[d]	64.9	±2.1	±1.1	13.3 ± 0.3

[a] Total pressure including 5 torr of SF_6. [b] With standard deviation. [c] *log A* with $\tau = 10^{-5}$ s; error limits discussed in text. [d] From ref 16; Δ *log A* (s^{-1}) = ± 0.2 assumed. [e] From ref 17. [f] Cf. last line.

peratures, i.e., various laser pulse energies. Moreover, the frequency factors A_1 and A_2 are related by

$$\ln A_1 = B + \frac{E_1}{E_2} \ln A_2 - \left(1 - \frac{E_1}{E_2}\right) \ln \tau \qquad (5)$$

Here the constant

$$B = \ln A_1 - \frac{E_1}{E_2} \ln A_2 + \left(1 - \frac{E_1}{E_2}\right) \ln \tau \qquad (6)$$

denotes the intercept of the plot ln $(k_1\tau)$ vs. ln $(k_2\tau)$ on the ln $(k_1\tau)$ axis. Thus, the Arrhenius parameters of the reaction of interest are obtained from a plot ln $(k_1\tau)$ vs. ln $(k_2\tau)$, provided E_1 is not too different from E_2.[12,14,15]

The results of four pyrolysis experiments are depicted in Figure 2. In each case we have selected a concerted, unimolecular elimination reaction as a reference. This reaction type is expected to reduce the possibility of side reactions. Table I summarizes experimental conditions, numerical results (slopes and intercepts) as derived by least-squares fits from Figure 2, the Arrhenius parameters of the reference reactions, and those found for the propynal and vinyl bromide decomposition.

The product yield of each educt pair investigated could be determined from the gas chromatogram in two ways. Either the remainder of educt 1 or that of educt 2 was used as a standard to calculate the absolute yield of C_2H_2. While both ways led to the same result in the case of the educt pair cyclopentene/vinyl bromide, small deviations were observed when propynal was one of the educts and high laser pulse energies were applied. Under these conditions additional products from propynal (<5% of propynal) introduced a small error. Therefore, we used only the educt compound admixed to propynal as an internal standard. The plots derived in this way (Figure 2) are linear throughout the region from low (i.e., ln $(k\tau) \ll 0$) to high laser pulse energies (ln $(k\tau) \sim 0$). It is noteworthy that here the product C_2H_2 is not subject to further reactions. In a separate experiment, a mixture of C_2H_2 with the sensitizer SF_6 was found to produce no detectable products even at the highest pulse energies employed in this work.

To assess the error limits of the measured activation energy of propynal, we considered the standard deviation of the slope in Figure 2 together with the uncertainty of the activation energy of the reference reaction. The pertinent data are listed in Table I. The errors of cyclopentene ($\Delta E = \pm 1$ kcal/mol)[16] and vinyl chloride (±2.9 kcal/mol)[17] were taken from the literature. Since the published kinetic data of vinyl bromide[18] are contradictory,[19] we preferred to reinvestigate the dehydrobromination by laser pyrolysis using the cyclopentene decomposition as a reference reaction. This result is also included in Table I.

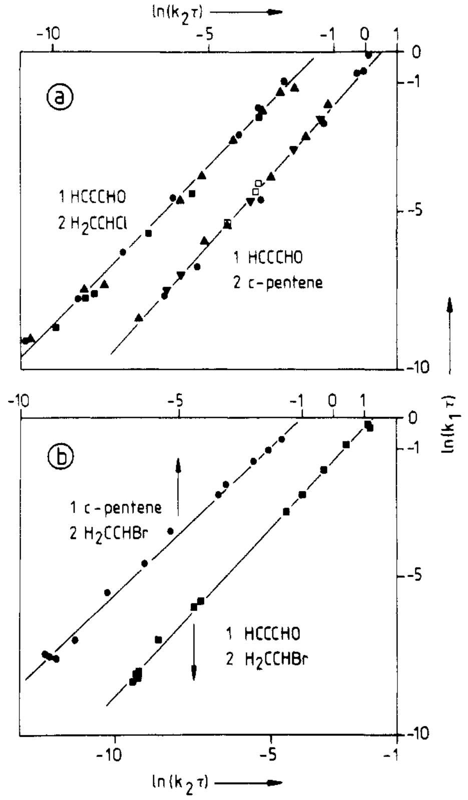

Figure 2. Plots ln $(k_1\tau)$ vs. ln $(k_2\tau)$ of the educt pairs propynal/vinyl chloride and propynal/cyclopentene (a) as well as cyclopentene/vinyl bromide and propynal/vinyl bromide (b). Note the two different abscissa scales for ln $(k_2\tau)$ in (b). The composition of the reaction mixtures is given in Table I.

The values obtained for the propynal reaction with cyclopentene, vinyl bromide, and vinyl chloride agree within the error limits ΔE (slope) and ΔE (reference). Taking into account both error sources, each propynal E value is estimated to be reliable within ±3 kcal/mol. However, the precision of the method is far better. Using cyclopentene as a common standard for the propynal and vinyl bromide reactions and subsequently vinyl bromide for the propynal decomposition, we obtained for the activation energy of propynal $E = 67.1$ and 67.7 kcal/mol, respectively. According to these results an average value $E = 68 \pm 2$ kcal/mol is considered the most reliable.

The frequency factor of the probe reaction (propynal and vinyl bromide) can be determined from eq 5, if the slope $E_1/E_2 = \mathrm{d} \ln (k_1\tau)/\mathrm{d} \ln (k_2\tau)$, the intercept B, the frequency factor of the reference reaction, and the reaction time τ are known. The error limits Δ log A (probe) with respect to B, A (reference), and τ were calculated with the slope given in Table I. The standard deviation ΔB and the values Δ log A (reference) are listed in Table I. The

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reaction time which is not known should at least be 10^{-6} s and shorter than 10^{-3} s. The lower limit is given by the laser pulse duration (~1.5 μs), and the upper limit corresponds to the time for heat flow from the irradiated region to the cold surroundings.[20] This cooling process was measured in a previous IR laser heating experiment[3] where the temperature-dependent phosphorescence of propynal was utilized to monitor the transient temperature. The findings are in good agreement with those of ref 12 and 15 which were based on IR fluorescence measurements. To be on the safe side, we considered the 10^{-6}–10^{-3}-s range as uncertainty and included it in Δ log *A* (cf. Table I). However, the largest error in *A* of propynal is due to the uncertainty of the *A* value of the reference.

Discussion

The laser pyrolysis experiments performed with three different standards provided three sets of Arrhenius parameters for the decarbonylation reaction of propynal. The results are listed in Table I. The activation energy is found to be 67–70 kcal/mol while the values log *A* (s^{-1}) lie between 13.9 and 14.8.

To discuss these figures, we first consider the conditions prevailing in our laser pyrolysis experiments and the assumptions underlying the data analysis. In this context the most pertinent factors are a fast thermalization of the laser energy, homogeneity of the gas-phase chemistry, and reaction conditions close to the high-pressure limit.[21]

Possible surface reactions were suppressed by keeping the reaction zone, which was mainly determined by the laser beam dimensions, sufficiently far from the cell walls and by repeated polishing of the NaCl windows. A fast intermolecular randomization providing the same temperature for the reactive probe and reference molecules was favored by using a sensitizer, SF_6. The direct photon absorption by probe or reference molecules was thus kept negligibly small. If one adapts the results of our previous study on sensitized TEA CO_2 laser heating of propynal[3] to the present conditions (1 torr of propynal + standard + 5 torr of SF_6), the thermalization of the absorbed laser energy is expected to be complete within 1 μs. To further improve thermalization and to bring the reaction conditions closer to the high-pressure limit, we added Xe as buffer gas. Its effectiveness was examined with the reaction system propynal/cyclopentene. Due to the relatively large difference of the parameters *E* and *A* between propynal and cyclopentene, this system appeared most sensitive to deviations from thermal conditions. The results of the experiments with 13 and 33 torr of Xe agree within experimental error and parallel that without buffer gas as shown in Figure 2. According to this finding, a total pressure of 20–25 torr (including 13–18 torr of Xe) was regarded high enough to provide a fast equilibration of the absorbed laser energy and low enough to furnish a sufficient chemical conversion for ≤3 h of laser irradiation time.

For each pair of probe and reference reactions used in this work the activation energies are within 6 kcal/mol (<10% of *E*) and the log *A* values within 1.1 (<10% of log *A*). Similar Arrhenius parameters of probe and reference reaction are very favorable, or even required, for the simple method of the data analysis given with eq 2–6.[12,15] While method and data handling are appropriate for determination of the activation energies, they might fail in providing accurate log *A* values. This situation arises when a strong deviation from the high-pressure limit prevails. Under this condition the activation energy is only slightly decreased but the frequency factor is reduced by several orders of magnitude.[21] If such a deficiency is considered, eq 2, 5, and 6 may be written as

$$\ln (k_1\tau) = \frac{E_1}{E_2}\ln (k_2\tau) + \ln A_1' - \frac{E_1}{E_2}\ln A_2' + \left(1 - \frac{E_1}{E_2}\right)\ln \tau \quad (7)$$

and

$$\ln A_1 = B + \frac{E_1}{E_2}\ln A_2 - \left(1 - \frac{E_1}{E_2}\right)\ln \tau + \frac{E_1}{E_2}\ln \alpha_2 - \ln \alpha_1 \quad (8)$$

with

$$B = \ln A_1' - \frac{E_1}{E_2}\ln A_2' + \left(1 - \frac{E_1}{E_2}\right)\ln \tau \quad (9)$$

where we have assumed that the *ratio* of the activation energies E_1/E_2 is the same in the falloff and the high-pressure regime. Deviations in the Arrhenius factor are approximated by the expression $A_1' = \alpha_1 A$ ($A_2' = \alpha_2 A_2$), *A* relating to the high-pressure value and *A'* to the effective one. The ratio A_1'/A_2' (or α_1/α_2) is assumed independent of the reaction temperature. Hence, a plot ln ($k_1\tau$) vs. ln ($k_2\tau$) of eq 7 furnishes E_1/E_2 as before, while the intercept *B* (eq 9) assumes a different physical meaning when compared with eq 6. Consequently, the determination of the activation energy is independent of this deficiency but not the value of A_1 as is evident from eq 8 and 5. Since it is difficult to establish α_1 and α_2,[21] we are left with an *A* factor determined from eq 5 subject to a considerable uncertainty. For the special case $E_1 = E_2$ the magnitude of this uncertainty is, according to eq 8, given by ln (α_2/α_1), the contribution for the reaction in the falloff regime. Taking this into account, it might not surprise to find the log *A* values of propynal determined with eq 5 in a wide range and too high relative to the values reported for unimolecular elimination reactions.[22]

Since the experimental value of the activation energy (68 kcal/mol) agrees within experimental error with the calculated energy barrier (69.9 kcal/mol), we preferred to determine the log *A* value with theoretical information. Based on the calculated energy, geometry, and vibrational frequencies of the transition state and on spectroscopic data of propynal in the electronic ground state, RRKM calculations with inclusion of tunneling corrections were previously performed.[7] These rate constants *k*(*E*) are now converted to *k*(*T*) according to

$$k(T) = \int_0^\infty k(E)\, N(E) e^{-E/kT}\, dE \Big/ \int_0^\infty N(E) e^{-E/kT}\, dE \quad (10)$$

where *N*(*E*) is the vibrational-state density at the energy *E* calculated with the same algorithm as used with the RRKM procedure. For temperatures of e.g. 1200 or 1800 K one finds

$$k(1200) = 2\ s^{-1} \qquad k(1800) = 3 \times 10^4\ s^{-1}$$

With a barrier height of 68 kcal/mol instead of 69.9 kcal/mol, *k*(*T*) increases by a factor of 3. Very similar values are obtained when the absolute rate theory is applied in conjunction with the transition-state geometry and its vibrations are taken from the ab initio calculation together with the spectroscopic data of the ground state.[7] According to the rate constants given above, the preexponential factor between 800 and 1800 K is $\bar{A} = 1.2 \times 10^{13}$ s^{-1}, a magnitude consistent with the "tight" transition state shown in Figure 3 (*cis*-$CTST_1$) and with the "narrow maximum" of the potential energy along the minimum-energy path around the transition-state geometry.

Considering the strong discrepancy between the theoretical (10^{13} s^{-1}) and experimental *A* value ($10^{14.4\pm0.5}$ s^{-1}), it is instructive to estimate the effective reaction temperature during pyrolysis. The values of ln ($k\tau$) given in Figure 2 and an assumed $\tau = 10^{-5}$ s provide reaction rate constants at various laser pulse energies. When these rates are inserted into the Arrhenius equation of the standard or the probe reactions using the kinetic parameters from Table I, respectively, one finds *T* = 1100–1600 K. Furthermore, at a sample pressure of ~20 torr and with a gas kinetic collision rate, the ratio $k_{coll}p/k(1600) \sim 10^8/10^5 \sim 10^3$ is obtained as the average value for these reactions. Compared with $k_{coll}p/k(T)$ of similar reactions,[21] this value is evidently not sufficient to bring the reaction conditions into the high-pressure limit. Since the

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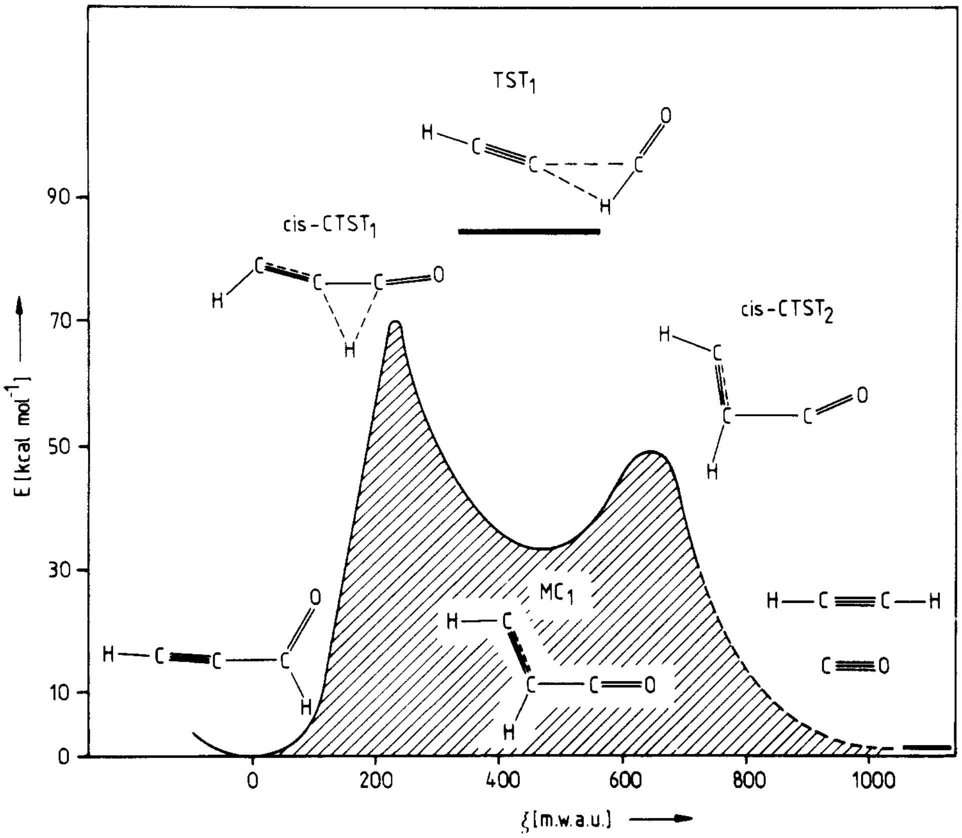

Figure 3. Calculated energy profile on the electronic ground-state surface of propynal along the lowest energy reaction coordinate ξ of the reaction HCCCHO → CO + HCCH.[7] The calculated geometries of the two transition states *cis*-CTST$_1$ and *cis*-CTST$_2$ and the metastable intermediate MC$_1$ are portrayed, together with the transition state TST$_1$ which belongs to the next higher reaction path with the same products. The energy scale refers to the vibrational ground state of propynal as origin; all values have been corrected for the zero-point energy.

available standard reactions show either lower activation energies or considerably higher A values than the propynal decarbonylation, a deviation from the high-pressure limit becomes severe.[15] Unfortunately, an appropriate pressure increase quenches the laser-induced chemical conversion to such a degree that accurate product analysis is no longer feasible.

In the light of the present information as well as of previous, detailed dynamic data the pertinent features of the decarbonylation reaction of propynal are summarized. As displayed in Figure 3, the lowest channel involves two transition states with a maximum barrier height of 68 kcal/mol. Disregarding a slightly higher (~2 kcal/mol according to the calculation in ref 6) pathway via the *trans*-CTST$_1$ transition state, the next higher channel is predicted to possess only one transition state (TST$_1$) at about 83 kcal/mol (86 kcal/mol without correction for the zero-point energy).[6,7] This reaction path bears some similarities with that of the formaldehyde decay $H_2CO \rightarrow H_2 + CO$, the activation barrier of which has been the subject of numerous calculations,[23] its most recent value being 80.9 kcal/mol.[24] The TST$_1$ reaction channel of propynal is characterized by fairly rigid HC≡C and H—C=O moieties while the lowest path proceeds via an energetically very favorable rearrangement (CTST$_1$) which involves most bond lengths and angles of the propynal frame. The subsequent potential barrier for CO elimination represented by CTST$_2$ is considerably lower and plays no role with respect to the reaction rate. The calculated decarbonylation path of propynal is a nearly thermoneutral reaction. Essentially the entire excitation energy goes into the fragments CO and HC≡CH. Moreover, the geometry of the second transition state, CTST$_2$, preceding the CO elimination, is strongly suggestive of nascent HC≡CH with a high degree of CH deformational excitation. In accord with this prediction, IR emission of the hot fragment CO[9] as well as from the excited H-deformation vibration ($\nu_4 + \nu_5$) in acetylene[25] has been monitored after $S_1 \leftarrow S_0$ excitation.

Conclusion

The method of comparative pyrolysis with pulsed IR laser excitation has been applied to molecular elimination reactions with activation energies up to 70 kcal/mol. The high reaction temperature thus required could conveniently be achieved by sensitized laser heating without interference from heterogeneous surface reactions. Moreover, the efficient polymerization reaction of propynal was entirely suppressed. Using three different reference reactions, we determined the activation energy of the decarbonylation reaction of propynal to a precision of ±2 kcal/mol. In spite of carefully chosen experimental conditions, the determination of the frequency factor failed. Comparing this result with the successful attempts performed on reactions having low activation energies, it is very likely that the high pyrolysis temperature prevents to provide the conditions (approach of the high-pressure limit) for an accurate evaluation of the A factor.

The good agreement between the calculated and the experimental activation energy lends further support to the predicted lowest energy path of the reaction HC≡C—CHO → HC≡CH + CO. Owing to the low activation energy of 68 kcal/mol, electronic excitation into the S_1 state followed by internal conversion provides for propynal an efficient doorway to enter the reaction channel under collision-free conditions.

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