

Photodissociation of acetaldehyde as a second example of the roaming mechanism

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Product state distributions of the CO produced in the 308-nm photolysis of acetaldehyde show clear evidence of two dissociation mechanisms. One is attributed to the conventional transition state mechanism predicted by theory, with high rotational and translational energy of the CO and a pronounced $v \perp J$ vector correlation. However, as much as 15% of the reaction flux proceeds via another pathway that produces low CO rotational and translational energy, very high CH₄ internal energy, and no correlation between the CO velocity and angular momentum vectors. The attributes of this channel are dynamically similar to the recently reported “roaming atom” mechanism in formaldehyde. We therefore speculate that the second pathway in acetaldehyde also occurs via a roaming mechanism in the CH₃ + HCO exit channel that decays into the CH₄ + CO channel.

photochemistry | photodissociation dynamics | product state distributions | roaming atom | transition state

The concept of the transition state (TS) is central to chemistry. It is the transient structure at the highest point of the minimum energy pathway (reaction coordinate) between reactants and products. Reaction mechanisms are often described with reference to this structure. For example, an S_N2 reaction is defined by the transient 5-center carbon atom at the TS, or a 3-center elimination reaction refers to the transient 3-membered ring at the TS. Interpretation of the kinetics and thermodynamics of reactions is also based on the energy and entropy of the TS—from the simplest Arrhenius model to more sophisticated TS theories, including their variational forms.

What would happen if reactions were found to bypass the TS? The result would be a new class of reaction mechanisms, with reaction products and kinetics that cannot be predicted by current TS theories. Recently, a mechanism of this type was reported, in which the photodissociation of H₂CO to H₂ + CO was observed to occur via a second, non-TS mechanism (1). The conventional 3-center elimination of H₂ from H₂CO has long been known to produce very high relative translational energy of the departing fragments, highly rotationally excited CO, and modest vibrational energy of the H₂ fragment (2). The new mechanism revealed a very different signature: rotationally cold CO, coupled with very high vibrational excitation of H₂ and low relative translational energy. The mechanism was interpreted by reference to quasiclassical trajectory calculations on a high-level *ab initio* potential energy surface (1). These calculations revealed that all of the reactions that produced the unusual signature circumvented the TS. The reaction starts out looking like a conventional C–H bond cleavage, which would produce the radical products of H₂CO photolysis: H + HCO. In a significant number of trajectories, just enough energy is tied up in internal motion of the HCO moiety so that the H-atom cannot quite escape; it turns back at very long distance (several angstroms) from the HCO but is still loosely bound. At this range, vibrational energy exchange is very inefficient and so the H-atom orbits the HCO. At some stage in the orbit it encounters the other H-atom and abstracts it from the HCO to produce very highly vibrationally excited H₂ and little vibration or rotation of the CO. This mechanism was referred to as the “roaming atom

mechanism.” What was surprising in the formaldehyde study was the relative importance of this mechanism in the overall reaction flux. Theory and experiment *both* demonstrated that the flux for the “roaming” mechanism increased with increasing excitation energy (1). At 25 kJ/mol above the threshold for “roaming,” as much as 30% of the CO + H₂ reaction flux was found to proceed via the roaming mechanism rather than over the TS.

Formaldehyde is the only molecule for which the roaming mechanism has been shown to have such a significant effect in the overall photodissociation. Formaldehyde holds a fairly unique place in photochemistry: it is among the smallest of systems that can produce polyatomic fragments, there is a moderately low density of states at the TS because of its small size and high vibrational frequencies, and also H-atoms would seem to be the most likely moieties to “roam” because of the large amplitude motion exhibited by vibrations involving hydrogen.

In this article, we test whether the importance of roaming mechanisms in chemistry is limited to formaldehyde, or other photochemically simple systems, by investigating the photodissociation of its larger cousin, acetaldehyde. Specifically, we have measured both the CO product state distributions at high resolution and their vector correlations. We explore whether there is any evidence for the signature of a roaming mechanism.

The photochemistry of acetaldehyde is far more complex than that of formaldehyde. Fig. 1 presents an energy level diagram showing the energetically accessible dissociation pathways and electronic states for excitation energies below ≈ 400 kJ/mol. The figure is constructed so that the “heavy” product channels: CH₃ + HCO and CH₄ + CO, both of which have been observed experimentally, are on the right. The two “light” fragment channels, H + CH₃CO and H₂ + CH₂CO, neither of which has been observed experimentally, are shown on the left. Two of these mechanisms, one on each side, are bond cleavage channels that produce radical products with no barrier to the reverse reaction. The other two mechanisms involve nuclear rearrangements to produce stable molecular products via a significant barrier. An observation that may prove to be crucial in later discussion is that the critical energy for all four channels is very similar: 360 ± 20 kJ/mol. It is also important to note that triple fragmentation, producing H + CO + CH₃, is energetically inaccessible at the energies used in this study.

Results

Laser-induced fluorescence spectra of the 0-0, 1-1, and 3-2 bands of CO were measured, probing population in $v = 0, 1,$ and 2 with full rotational resolution. The intensity of each line was mea-

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Abbreviation: TS, transition state.

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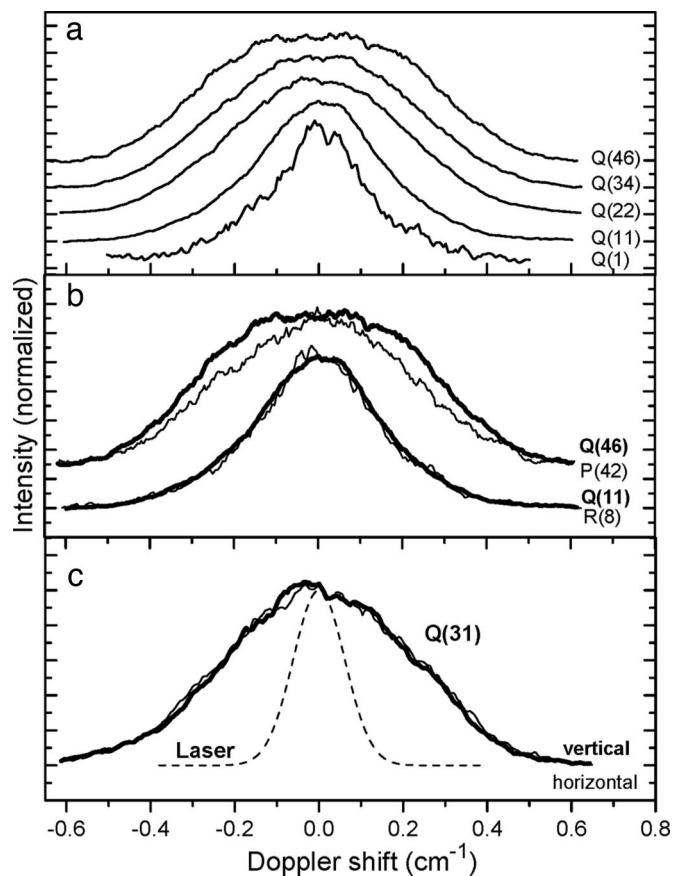


Fig. 3. Doppler profiles of a variety of rotational lines in the 0–0 band of CO. Vertical displacement of some lines is for clarity. (a) Lines broaden with increasing rotational excitation. (b) Flattening of the Q profiles in comparison with the P or R profiles. (c) No difference with polarization of the probe laser with respect to the photolysis laser. The laser linewidth is shown as a dashed line.

low translational energy, no v - J correlation, and very high internal energy of the CH_4 fragment. The relative flux for each mechanism can be obtained by integrating the high- J Gaussian fits to the data in Fig. 2, which yields 85% for Mechanism A and 15% for Mechanism B.

Discussion

There have been several *ab initio* calculations of the potential energy surface leading to $\text{CH}_4 + \text{CO}$ production from acetaldehyde; each shows a 3-center TS with the aldehyde H-atom bridging the two C-atoms (see Fig. 1) (6–10). Quasiclassical

trajectory calculations have been carried out on one of these potential energy surfaces (9, 10), albeit with reaction energy 94 kJ/mol ($7,800 \text{ cm}^{-1}$) above the reaction energy in these experiments. These calculations show that CO is produced with a symmetric, Gaussian distribution peaked at $J \approx 57$ (10). CO vibrational excitation is modest because the CO bond length at the TS is similar to that of free CO. There is considerable translational energy in the products. However, the internal energy of the CH_4 is most highly populated with $\approx 52\%$ of the available energy. Finally, the v - J vector correlation was also reported from the quasiclassical trajectory calculations (9), which showed almost perfect $v \perp J$ alignment for dissociation via the 3-center TS.

All aspects of the trajectory study are in at least qualitative agreement with the distributions we have labeled as Mechanism A: moderately high CO rotation, low CO vibration, high relative translation, high CH_4 internal energy, and a high $v \perp J$ alignment. To better facilitate comparison of the experiment and theory at quite different initial energies, we report percent disposal into each degree of freedom in Table 1. The average disposal of energy in all degrees of freedom as well as the alignment data are found to be in semiquantitative agreement. Not only are the averages in good agreement, but the shape of the experimental and theoretical distributions, where available, also agree. We therefore attribute Mechanism A to the conventional reaction over the 3-center TS, as modeled by the theory.

The other mechanism, B, exhibits a set of product state distributions that are qualitatively and quantitatively different. Table 1 reports the average energy disposal into each degree of freedom for this mechanism, again as a percentage of the available energy to facilitate comparison with Mechanism A and the trajectory calculations. The percent energy disposal shows low CO vibration, very low CO rotation, low relative translation, and, by conservation of energy, very large internal energy in the CH_4 sibling fragment. There is also effectively no correlation between the velocity and angular momentum vectors. These features are not found in the theoretical studies of TS dynamics and so we conclude that CO products associated with this distribution of energy must arise from a different mechanism. Fig. 1 shows all other known or postulated pathways for acetaldehyde photolysis at energies below 400 kJ/mol. None of these includes CO as a product. The only other known channel involving CO is the triple fragmentation into $\text{CO} + \text{CH}_3 + \text{H}$, also shown in Fig. 1, but this channel is inaccessible in these experiments by $\approx 25 \text{ kJ/mol}$.

The CO rotational distributions reported here for Mechanism B are quite similar to the CO rotational distributions observed in the photodissociation of formaldehyde (2). In that study, when the photolysis energy was below the threshold for the radical $\text{H} + \text{HCO}$ channel, the CO distribution was also Gaussian, and peaked at high J . As the photolysis energy was raised above the onset of the radical channel, a new, low J feature emerged in the

Table 1. Characteristics of the two identified mechanisms for CO production

Mechanism	Energy (kJ/mol)*				Alignment deg. $v \perp J$	Fraction of flux
	Translation	CO rotation	CO vibration	CH_4 vibration/rotation		
A	High (101)	High (39)	Low (10)	High (253)	High	85%
	25%	10%	3%	63%	0.7 ± 0.3	
Theory†	32%	13%	3%	52%	1.0	—
B	Low (43)	Very low (3)	Low (5)	Very high (352)	Low	15%
	11%	0.5%	1.5%	87%	0	

Mechanism A is identified as the regular TS mechanism by comparison with theoretical calculations (10). Mechanism B is attributed to a roaming mechanism. $E_{\text{avail}} = 403 \text{ kJ/mol}$.

*Percentages are relative to the total available energy.

†Ref. 10.

CO rotational distribution. This has now been interpreted as the opening up of the “roaming atom” mechanism (1).

A critical factor in the elucidation of the roaming mechanism in H_2CO was the observation that CO fragments in the low J (roaming) part of the distribution were also recoiling slowly (1). This is the same as we observe here for the low J CO molecules in Mechanism B. In formaldehyde, the roaming mechanism was associated with very high vibrational energy of the partner H_2 fragment. Table 1 shows that the partner CH_4 fragment from acetaldehyde has $\approx 87\%$ of the available energy, which should be mostly vibrational energy as discussed above. The only possible discrepancy is that the CO rotational distribution from acetaldehyde, peaking at $J = 30$, is somewhat colder than that for formaldehyde, which peaks at $J = 45\text{--}50$. From an impulsive model, one might reasonably expect the CO rotational distribution for acetaldehyde to be hotter than that for formaldehyde, but the fact that CH_4 can absorb substantial internal energy makes a simple impulsive model less applicable to acetaldehyde. Indeed, calculations show that the CH_4 internal energy, 52% of the total in acetaldehyde (10), is much higher than the H_2 internal energy, $\approx 25\%$ of the total in formaldehyde (1).

The Mechanism B distributions therefore appear to be similar in all regards to product state distributions for the “roaming atom” mechanism in H_2CO (1, 2). Because of these similarities, we explore the possibility that a similar mechanism might be at play here. Using H_2CO as a guide, it appears that what is needed is a simple bond cleavage channel to radicals at an energy similar to that of the top of the TS. A similar energy barrier is required because, if the interacting channel were too high or low in energy, the reaction flux through the lower energy channel would dominate. Fig. 1 shows that there are two such simple bond cleavage pathways producing radicals in acetaldehyde. Both have no exit barriers and are within 15 kJ/mol of the calculated height of the TS (6, 9), and therefore both are good candidates on the basis of energy.

We can now speculate about which roaming mechanism might lead to the observed results. The higher-energy pathway ($\text{CH}_3\text{CO} + \text{H}$) would lead to a roaming mechanism that is conceptually similar to the H_2CO case, with a roaming H-atom abstracting a methyl group from the acetyl fragment. This mechanism has some attraction in that it is the light H-atom that is roaming the periphery of the complex, but there are also difficulties. The methyl group is sp^3 hybridized in acetyl, and

therefore the H-atom has no ready site of attack to abstract it from CO.

The lower-energy pathway ($\text{CH}_3 + \text{HCO}$) would involve the methyl and formyl groups orbiting each other, with the CH_3 abstracting an H-atom from HCO. The attraction of this pathway is that both fragments can tie up some of the excess reaction energy to prevent simple dissociation. Also, at such long distances as required for a weakly bound complex, the methyl would be planar and sp^2 hybridized, and would readily abstract the exposed H-atom on the formyl group. We favor this mechanism, but clearly theoretical support would be needed to decide between the two mechanisms.

Conclusions

In conclusion, we have presented detailed product state distributions of the CO produced in the 308-nm photolysis of CH_3CHO . These distributions show clear evidence of two mechanisms for CO production. One of these mechanisms is the conventional TS mechanism. However, as much as 15% of the reaction flux proceeds via another pathway that is dynamically very distinct. We attribute this other mechanism to a roaming mechanism in the $\text{CH}_3 + \text{HCO}$ channel that decays into the $\text{CH}_4 + \text{CO}$ exit channel. It is dynamically similar to the recently reported “roaming atom” mechanism in formaldehyde.

Experimental Procedures

A 5% mixture of acetaldehyde vapor in He was expanded via a pulsed nozzle into a vacuum chamber. Supersonically cooled acetaldehyde molecules (15 K) were photolysed ≈ 10 mm downstream by an excimer laser at 308 nm. The nascent CO reaction products were detected 50–200 ns later by laser-induced fluorescence via the $A\text{--}X$ transition in the region 140–160 nm. The vacuum UV radiation was generated in Mg vapor by 4-wave mixing, the full details of which have been published previously (14). CO fluorescence was imaged directly onto a solar blind photomultiplier attached to the chamber.

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