THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2008, *112,* 7489–7491
Published on Web 07/25/2008

The Photochemistry of Formaldehyde: Internal Conversion and Molecular Dissociation in a Single Step?

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Received: April 11, 2008; Revised Manuscript Received: June 3, 2008

A novel, nonadiabatic reaction path for H_2 + CO molecular dissociation of formaldehyde via an extended S_1/S_0 conical intersection seam has been mapped out using the CAS-SCF method with a full valence active space (10 electrons, 9 orbitals). Two conical intersection geometries have been optimized, CsCoIn, a saddle point in the intersection space, and C1CoIn, which is the lowest-energy crossing point. A minimum-energy path connecting these points along a seam has also been characterized. In addition to the conventional and "roaming-atom" mechanisms—where internal conversion takes place before ground-state dissociation—we suggest that a strictly nonadiabatic mechanism can operate, where internal conversion and dissociation take place in concert.

Formaldehyde photochemistry has a long history.[1] It is observed that photoexcitation of the S_1 (n−π^*) state can lead to loss of H_2 (molecular dissociation, the focus of this paper) or loss of H (radical dissociation). At low energies, CO rotation is detected, while at higher energies, rotationally cold CO and vibrationally hot H_2 are produced. The branching ratio between these two channels is a continuous function of the excess energy.

The accepted mechanisms for the molecular dissociation are two-step. An early S_1/S_0 radiationless decay (internal conversion) produces hot vibrational states of bound S_0 formaldehyde and is followed by S_0 dissociation of the equilibrated system. (More energetic channels involving intersystem crossing with the T_1 state will not be discussed here.) Two mechanisms have been suggested to rationalize the two competitive channels. At low excess energy, channel 1 proceeds via an S_0 transition state (TS), a skewed molecular structure that preconditions CO rotation (conventional molecular mechanism). At higher excess energies, H atom dissociation is not complete, and the partially dissociated H atom reattaches itself, populating hot vibrational states of H_2. This "roaming-atom" mechanism,[1a–e] called channel 2, corresponds to a spectrum of dynamical pathways that are far from the minimum-energy path and thus can bypass the S_0 TS of channel 1. This interpretation is supported by classical trajectory calculations[1b] that have confirmed the experimental distribution of energy into the products.

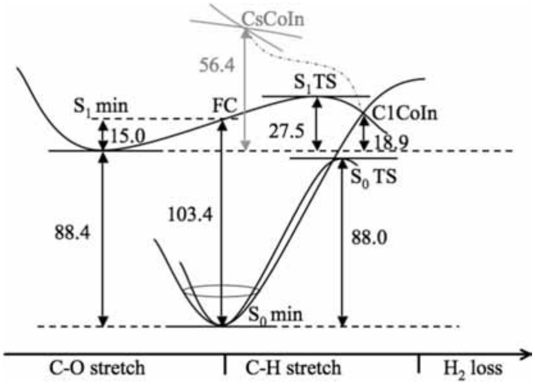

Figure 1. Relative energies (in kcal mol^{-1}) of and connections between the formaldehyde S_0 and S_1 critical points. The dash−dotted line is the seam connecting CsCoIn to C1CoIn (Figure 3).

The received view does not involve any conical intersection, and the Fermi golden rule is invoked to justify decay at geometries where the electronic energy gap is large, compensated by a large density of bound S_0 vibrational states. In contrast, we document here an additional mechanism where S_1/S_0 radiationless decay and molecular dissociation take place simultaneously via an S_1/S_0 conical intersection (CoIn) located beyond an S_1 TS on the way to the products. This corresponds to an explicit nonadiabatic reaction path, $S_1(FC) \rightarrow S_1(min) \rightarrow S_1(TS) \rightarrow S_1/S_0$ CoIn → CO + H_2 (Figure 1), where the S_1 TS correlates diabatically to the S_0 dissociation products through the conical intersection. The corresponding molecular structures (see Supporting Information) are very similar to those along the ground-state path, $S_0(min) \rightarrow S_0(TS) \rightarrow$ CO + H_2, related to channel 1 (Figure 1). Further, since there is a minimum and a transition state on S_1, preceding the conical intersection, the system will become quasi-equilibrated prior to radiationless decay, which will not be ultrafast (the rate-limiting step relates here to the S_1 transition barrier).

The energy and geometry at which S_1 and S_0 are degenerate correspond to an extended S_1/S_0 conical intersection seam.[2] We have found a new low-energy conical intersection point, C1CoIn (Figures 1 and 2), as well as a structure at much higher energy,[1f] CsCoIn (Figures 1 and 2). We have also characterized a continuous line (seam) of crossing geometries linking the two points (Figures 1 and 3). Remarkably, decaying from S_1 to S_0 along the extended seam also supports the experimental

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10.1021/jp803152g CCC: $40.75

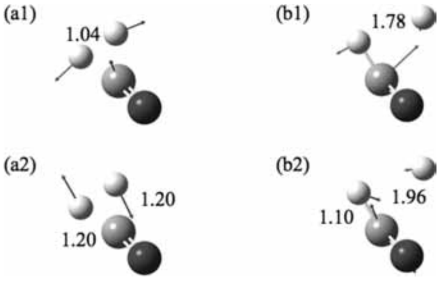

Figure 2. Optimized structures and branching-plane vectors on the S_1/S_0 (n−π*) conical intersection seam; (a) CsCoIn, (b) C1CoIn, (1) gradient difference, (2) derivative coupling. CH and HH bond lengths are shown in Å.

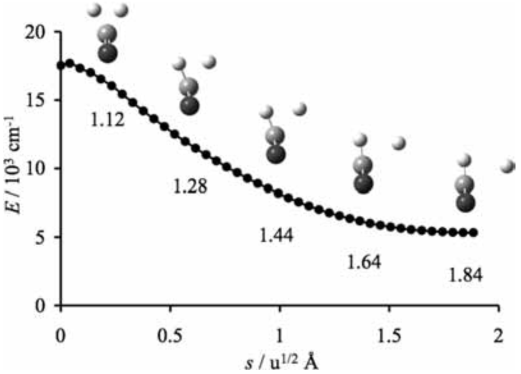

Figure 3. Seam MEP linking CsCoIn to C1CoIn. The HH bond length is quoted in Å for five selected structures. Energies refer to the S_1 minimum.

observation that H_2 gets vibrationally hotter when the excess energy increases, as further explained below.

In our computations, the energies and optimized structures have been obtained with a full valence active space (10 electrons, 9 orbitals) and a 6-31G* basis set. This includes a part of the dynamic electron correlation (CO $\sigma \rightarrow \sigma^*$). All analytical frequency computations and MEPs (minimum-energy paths) were carried out with a reduced CAS (8,7) active space, at reoptimized geometries. This leaves out a pair of CH_2 σ, σ^* orbitals and does not affect the structure or energetics significantly.

In ref 1g, Feller et al. discuss benchmark energetics for the ground-state surface. Their best estimate of the vibrationless (without ZPE correction) S_0 barrier height is 87.4 kcal mol^{-1}. Our estimate (no ZPE correction, Figure 1) is 88.0 kcal/mol (0.6 kcal mol^{-1} higher). If we use their ZPE correction (−5.5 kcal mol^{-1}), we get a value of 82.5 kcal mol^{-1}, which is 3.3 kcal/mol higher than the experimental 79 kcal mol^{-1}.[5a] The experimental S_0 to S_1 adiabatic and vertical excitation energies are 81 and 94 kcal mol^{-1},[5a–c] 7−9 kcal mol^{-1} lower than our values (Figure 1). Such errors could be corrected by including additional dynamic electron correlation, but since our objective is mechanistic, we are confident that our results are accurate enough for this purpose.

The geometries of the CsCoIn and C1CoIn conical intersection points are shown in Figure 2 along with the vectors characterizing the branching plane (where the degeneracy is lifted). The geometry of CsCoIn is similar to the one reported in ref 1f. Notice (Figure 2, b2) that a CH distance in C1CoIn is rather large (1.96 Å), so that this geometry might be described as quasi-radicaloid (H•····•HCO) or even "roaming-atom"-like.[1] As pointed out in ref 1f, CsCoIn is too high in energy to be accessible. However, the energy of C1CoIn is only 4.9 kcal mol^{-1} higher than the FC excitation energy (Figure 1).

Using a recently developed method[3] (implemented in ref 4), we have characterized CsCoIn as a saddle point in the intersection space (orthogonal to the branching-plane vectors shown in Figure 2) with an imaginary frequency of 2277i cm^{-1}. Following this mode,[3] we have mapped out a seam MEP from CsCoIn to C1CoIn within the intersection space (where the energy remains degenerate). The energy and selected geometries are shown in Figure 3. This computed seam MEP demonstrates that CsCoIn and C1CoIn are optimized points on the same extended S_1/S_0 conical intersection seam.

We have also computed four conventional S_0 MEPs: (i) leading to H_2 dissociation from the S_0 TS, (ii) from the two optimized S_1/S_0 conical intersection points, and (iii) from a point midway along the seam MEP (Figure 3). (Movies of all of the MEPs, together with animations of the vectors in Figure 2, can be found in the Supporting Information.) In the case of S_0 MEPs from a conical intersection point, the initial displacement direction was chosen to be either of the branching-plane vectors in Figure 2. All start at a longer CH distance than the MEP from the S_0 TS (Figure 1) but lead to the same dissociation products, CO + H_2. This suggests that the conical intersection seam lies beyond (Figure 1) the S_0 TS along the dissociation coordinate. Thus, in addition to the S_0 mechanisms, a nonadiabatic mechanism involving the S_1/S_0 conical intersection seam can operate as well. The S_1 TS, which lies on the way to the seam, has a very similar geometry to the S_0 TS and controls the dissociation rate in a similar way but on a different electronic state. The extent to which the direct nonadiabatic mechanism proposed here operates depends on the relative time scale and efficiency of tunneling through the corresponding barrier, compared to that of the internal conversion from S_1 to S_0.

The energies involved in stimulating the CO rotation are so small that accurate predictions must await dynamics computations. However, the energy distribution into HH vibration upon radiationless decay to the ground state at these points can be related qualitatively to the structures on the conical intersection seam (Figure 3). The system can evolve on S_1 to C1CoIn with only a slight change in HH distance from the S_1 FC point. The HH distance in ground-state formaldehyde is 1.88 Å. It is 1.79 Å at the S_1 TS and 1.78 Å at CsCoIn. In contrast, the HH distance is dramatically compressed at CsCoIn (1.04 Å). Further, one can see from Figure 3 that the HH distance decreases continuously along the seam MEP. Thus, the central mechanistic point is that, as the excess energy is increased, decay will occur at points along the seam from which HH vibration is increasingly stimulated, as observed experimentally.

The branching-plane vectors (Figure 2) reinforce this conjecture. At the higher-symmetry CsCoIn, the gradient difference is a HH stretch/HCH scissor movement (Figure 2, a1). Thus, this vibration will become enhanced as the molecule decays to S_0 nearer to this conical intersection point. (The derivative coupling vector corresponds to a HCH asymmetric stretch.) In contrast, at the C1CoIn point, the degeneracy lifting coordinates are dominated by HCO in-plane (Figure 2, b1) and out-of-plane bends (Figure 2, b2) that could lead to CO rotation in a product.

In summary, we have characterized two limiting, strictly nonadiabatic mechanisms, $S_1(FC) \rightarrow S_1(min) \rightarrow S_1(TS) \rightarrow S_1/S_0$ (CsCoIn or C1CoIn) $\rightarrow$ CO + H_2, for formaldehyde, which are continuously transformed into each other along an extended conical intersection seam. Changeover from CO rotation to HH vibration in the products can occur along a continuous spectrum of reaction pathways accessible via the S_1/S_0 seam. The extent of involvement of these nonadiabatic mechanisms, compared to the ground-state conventional and "roaming-atom" mechanisms, depends on the time scale and efficiency of the internal conversion from S_1 against those of tunneling through the S_1 transition barrier, which is a question for future nonadiabatic quantum dynamics studies.

Acknowledgment. Support from FCT-Portugal (Grant No. SFRH/BD/36197/2007) and the EPSRC-UK (Grant No. EP/F028296/1) is acknowledged. We thank Dr. Fabrizio Sicilia for developing code used here and for earlier calculations on formaldehyde with Roshan Samarasinghe.

Supporting Information Available: Full citation of Gaussian (ref 4); geometries and energies of all critical points; animations of the vectors in Figure 2; the seam MEP; and S_0 MEP from the S_0 TS, CsCoIn, C1CoIn, and a point midway along the seam MEP. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP803152G