Supporting information:

Quantitative Integral Cross Sections for the H + CO_2 → OH + CO Reaction from a Density Functional Theory-Based Potential Energy Surface

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Details of the *Grow* method as applied to HOCO

In this work, a two-part weight function has been used, with the parameters set to $q = 2$ and $p = 12$. To define the confidence lengths in the weight formula, the number of nearest neighbors was chosen as 48, and the error tolerance was taken to be $2\mathrm{x}10^{-4}$.

In practice, the points on the PES are generated iteratively. The initial data set is composed of 122 points and has been constructed at and close to the stationary points and reaction paths of the reaction. Then, a sufficient number of QCT trajectories are run simultaneously. To ensure at least some reactive events, the trajectories are initiated using microcanonical distributions of the ground rovibrational states of reactants, H + CO_2 (with energies 0 and 0.012 au) and products, OH + CO (with energies 0.0085 and 0.0051 au, respectively), at the following collision energies: 0.044, 0.055, 0.066, 0.077, and 0.088 au (1.2, 1.5, 1.8, 2.1, and 2.4 eV) for the direct reaction, and 0.0037, 0.011, 0.018, and 0.026 au (0.1, 0.3, 0.5, and 0.7 eV) for the reverse reaction. The vibrational energies are approximately zero-point energies and the collision energies correspond approximately to those where experimental data are available. Impact parameters are set to 3.5 and 4.5 a_0 for the direct and reverse reaction, respectively, and the initial separation of the reactant and product molecules is set to 15.0 a_0. A sample of the configurations visited by both reactive and non-reactive trajectories is recorded. One data point is selected alternatively from the "variance sampling" and "h-weight" methods,[1] and it is added to the potential file. Trajectories are run again on the new PES and the process is repeated, monitoring the convergence of the reaction probabilities (impact parameter equal to zero) of the direct and reverse reactions at all energies every time 200 new data points are added, starting with a PES with 800 points. In total, 1600 points are considered sufficient to achieve a reasonably converged PES. To remove an artificial minimum with energy below that of the absolute minimum on the

PES (which corresponds to the *trans*-HOCO minimum), 44 more points were added with trajectories run at a single 0.1 eV collision energy for the reverse reaction. Thus, the final PES comprises 1644 data points.

During the PES construction, it was found necessary to perform UHF/aug-cc-pVTZ calculations of the energy at every point, and then to give the resulting orbitals as initial orbitals for the M06-2X/aug-cc-pVTZ calculations. This was done to ensure proper convergence of the energy, first, and second derivatives computed at the M06-2X/aug-cc-pVTZ level at long separation distances of the reactant and product molecules. All *ab initio* calculations were performed with the MN-GFM (Minnesota Gaussian Functional Module) version 4.1[2] modified version of Gaussian 03,[3] which includes the M06 family of density functionals. Also, an integration grid of 250 radial points and 590 angular points, more extended than the standard “ultrafine” grid of Gaussian 03, was defined to avoid irregularities in the M06-2X energies and derivatives.[4]

The convergence of the PES as a function of the number of points in the data set is shown in Fig. S1. As can be seen, the final PES (1644 points) and the previous one (1400 points) have reaction probabilities situated essentially within their mutual error bars at all collision energies for the title reaction, and at all collision energies except 0.3 eV for the reverse reaction. We deem this level of convergence sufficient, as the reaction probabilities are all very small, below 3%. Also, all the potential energies in all trajectories are above the one of the absolute minimum. Thus, apparently the PES does not present artificial low-energy minima.

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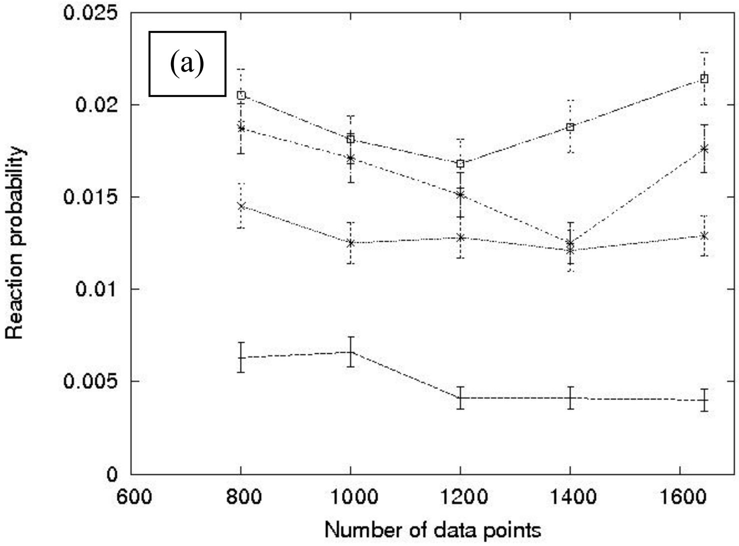

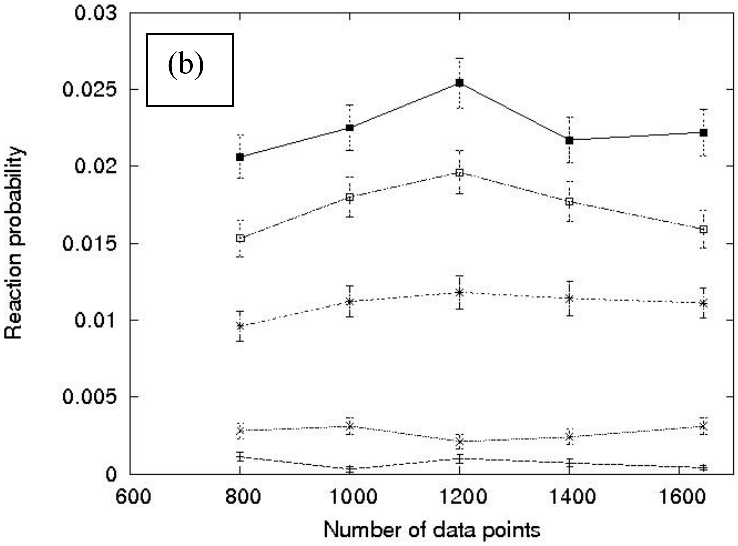

Figure S1: Reaction probability for the different collision energies of the (a) OH + CO → H + CO_2 and (b) H + CO_2 → OH + CO as a function of the number of data points present in the potential file. In order of increasing reaction probability, we have (a) 0.1, 0.3, 0.5, 0.7 eV; (b) 1.2, 1.5, 1.8, 2.1, 2.4 eV. Results correspond to 10000 trajectories per energy, with error bars representing one standard deviation.

Table S1. Classical energies of stationary points (eV) on the ground-state HOCO PES, relative to OH + CO. For selected stationary points the energies are given relative to H + CO_2 (italic in parentheses).

Species	M06-2X a)	CCSD(T) b)	FCC/CBS c)	HEAT d)	CCSD(T)-F12
OH + CO	0.0 (*1.045*)	0.0 (*0.960*)	0.0 (*1.014*)	0.0 (*1.022*)	0.0 (*0.981*)
OH.CO	–0.0900	–0.0910	–0.0952	–0.112	–0.0980
OH.OC	–0.0476	–0.0497	–0.0489	–0.0365	–0.0529
trans-TS1	–0.0334	–0.0287	–0.0416	–0.0273	–0.0252
cis-TS1	0.138	0.136	0.114	—	0.135
trans-HOCO	–1.365	–1.262	–1.305	–1.277	–1.283
cis-HOCO	–1.303	–1.184	–1.225	–1.203	–1.206
τ-HOCO	–0.970	–0.857	–0.901	–0.874	–0.880
cis-TS2	0.00816 (*1.053*)	0.126 (*1.086*)	0.0624 (*1.076*)	0.108 (*1.130*)	0.105 (*1.086*)
TS4	0.298 (*1.343*)	0.409 (*1.369*)	0.341 (*1.355*)	0.387 (*1.409*)	0.381 (*1.362*)
HCO_2	–0.623 (*0.422*)	–0.570 (*0.390*)	–0.632 (*0.382*)	–0.558 (*0.464*)	–0.557 (*0.424*)
TS3	–0.441 (*0.603*)	–0.354 (*0.606*)	–0.427 (*0.587*)	–0.356 (*0.666*)	–0.378 (*0.603*)
H + CO_2	–1.045 (*0.0*)	–0.960 (*0.0*)	–1.014 (*0.0*)	–1.022 (*0.0*)	–0.981 (*0.0*)
trans-TS2	0.838 (*1.883*)	1.073 (*2.033*)	—	—	—
c-c-TS	0.776	0.909	—	—	0.885
c-t-TS	0.833	1.110	—	—	—
S1	–0.220	0.002	—	—	—

a)M06-2X/aug-cc-pVTZ, present work.

b)CCSD(T)/aug-cc-pV5Z//M06-2X/aug-cc-pVTZ, present work

c)Ref. 5.

d)Ref. 6.

e) Ref. 7.

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