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The HCO₂ potential energy surface: Stationary point energetics and the HOCO heat of formation

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The energies of six stationary points on the OH+CO→HOCO→H+CO₂ potential energy surface have been calculated using the G3 and CBS-QB3 methods. An analysis combining *ab initio* and experimental enthalpies yielded $\Delta H_f^{298\text{ K}}(\textit{trans}\text{-HOCO}) = -42.9 \pm 1.5 \text{ kcal mol}^{-1}$ ($-43.8 \pm 1.4 \text{ kcal mol}^{-1}$) at the G3(CBS-QB3) level of theory. These results confirm the revised HOCO heat of formation derived from photoionization spectroscopy and suggest that the HOCO potential well is $8.8 \text{ kcal mol}^{-1}$ shallower than previously thought. We discuss the implications of these results for accurate Rice–Ramsperger–Kassel–Marcus modeling or quantum mechanical scattering calculations of the OH+CO reaction. © 2000 American Institute of Physics.

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The OH+CO→HOCO→H+CO₂ reaction has been the subject of extensive experimental^{1–6} and theoretical^{7–14} investigation due to its importance in atmospheric chemistry, in combustion, and as the prototypical complex-forming bimolecular reaction. The crucial role played by the HOCO intermediate in determining the reaction dynamics has been emphasized by crossed molecular beam scattering measurements,¹ femtosecond laser detection of the product evolution,^{5,6} measurements of the differential cross sections for the H+CO₂ reaction,^{15–17} and the observation of scattering resonances in calculations of the quantum mechanical reaction probability.^{9–14} The wealth of data available for this system has made it a benchmark for the study of four-atom reaction dynamics.

Despite widespread interest in the OH+CO reaction, the energetics of the HCO₂ potential energy surface remain poorly defined. Figure 1 illustrates that the reaction proceeds from OH+CO over a negligibly small barrier at TS1, into the potential well containing both *cis*- and *trans*-HOCO conformers, then over the TS2 barrier to H+CO₂. The experimental enthalpies¹⁸ of the OH+CO entrance channel and the H+CO₂ exit channel provide absolute reference points for the characterization of the entire potential surface. Analysis of reaction rate data has produced general agreement that TS2, the [H⋯OCO] transition state, lies 1–2 kcal mol⁻¹ above the zero point energy of the OH+CO entrance channel,^{2–4} but the exact energy of TS2 has not been definitively established. The HOCO well depth had long been accepted as $35.4 \text{ kcal mol}^{-1}$ based on the $\Delta H_f^{298\text{ K}}(\textit{trans}\text{-HOCO}) = -52.5 \text{ kcal mol}^{-1}$ derived from photoionization measurements¹⁹ and corroborated by *ab initio* calculations.⁸ However, reanalysis of the threshold region of the photoionization spectra^{20,21} recently led to the conclusion that $\Delta H_f^{298\text{ K}}(\textit{trans}\text{-HOCO}) \geq -46.5 \text{ kcal mol}^{-1}$, or that the HOCO well depth extends no more than $29.4 \text{ kcal mol}^{-1}$ below the OH+CO asymptote. Such a large change in the

HOCO well depth has significant consequences for the existing literature on OH+CO rate calculations since the most sophisticated Rice–Ramsperger–Kassel–Marcus^{3,4} and quantum mechanical scattering calculations^{8–10,13,14,22} employed the 35 kcal mol^{-1} well depth. The possibility of significant errors in the energetics of the key stable points of the empirical potential surface^{8,9,12,22} suggested that there might be more subtle energetic discrepancies for other regions of the potential. Therefore, we began an *ab initio* characterization of the full six-dimensional HCO₂ potential energy surface with the goal of determining a chemically accurate potential. Here we report accurate energies for the key stationary points.

The HCO₂ stationary point energies have been calculated using the CBS-QB3²³ and G3²⁴ model chemistries. These methods produce results that deviate from experimental heats of formation by mean absolute values of 0.87 and $1.02 \text{ kcal mol}^{-1}$, respectively. Stationary point structures were optimized at the B3LYP/6-311++G(3df,3pd) level of theory. The optimized structures agreed with published values⁸ and were used as the starting points for CBS-QB3 and G3 calculations. Thermochemical quantities for the HOCO stationary points have been calculated both at 298.15 and 0 K; Table I lists the results. To facilitate comparison with existing thermochemical information, Table II presents enthalpies of each stationary point relative to the enthalpy of OH+CO. Note that the *ab initio* reaction enthalpies for OH+CO→H+CO₂, $\Delta H_{r \times n}^{298\text{ K}}(\text{G3}) = -24.9 \text{ kcal mol}^{-1}$ and $\Delta H_{r \times n}^{298\text{ K}}(\text{CBS-QB3}) = -25.4 \text{ kcal mol}^{-1}$, reproduce the experimental value¹⁸ $\Delta H_{r \times n}^{298\text{ K}} = -24.85 \text{ kcal mol}^{-1}$ within $0.6 \text{ kcal mol}^{-1}$.

We combined the *ab initio* results from Tables I and II with the experimental enthalpies for OH+CO and H+CO₂ to generate two determinations of $\Delta H_f^{298\text{ K}}(\textit{trans}\text{-HOCO})$ for each model chemistry. These results are collected in Table III. The experimental uncertainties in the OH, CO, H, and CO₂ thermochemistry¹⁸ are negligible compared to the estimated uncertainties in the HOCO energetics. The uncertain-

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TABLE I. *Ab initio* energies (hartrees) for the HCO₂ potential surface.

	OH	CO	OH+CO	<i>t</i> -HOCO	TS3	<i>c</i> -HOCO	TS2	H+CO ₂	H	CO ₂
0 K										
CBS-QB3	-75.649 693	-113.182 257	-188.831 950	-188.872 480	-188.859 555	-188.869 239	-188.830 252	-188.871 831	-0.499 818	-188.372 013
G3	-75.694 906	-113.267 368	-188.962 274	-189.000 974	-188.988 103	-188.997 986	-188.962 205	-189.001 301	-0.501 003	-188.500 298
Expt	38.39	-113.81	-75.42	-191.6				-177.116	216.035	-393.151
(kJ/mol) ^a										
298 K										
CBS-QB3	-75.646 388	-113.178 952	-188.825 340	-188.868 314	-188.855 569	-188.865 101	-188.826 073	-188.865 897	-0.497 457	-188.368 440
G3	-75.691 601	-113.264 063	-188.955 664	-188.996 766	-188.984 124	-188.993 829	-188.958 007	-188.995 372	-0.498 642	-188.496 730
Expt	38.987	-110.53	-71.543	-194.6				-175.523	217.999	-393.522
(kJ/mol) ^a										

^aExperimental enthalpies taken from Refs. 18 and 21.

ties listed for each determination of $\Delta H_f^{298\text{ K}}$ (*trans*-HOCO), 1.5 kcal mol⁻¹ for CBS-QB3, and 1.8 kcal mol⁻¹ for G3, are dominated by the uncertainties from the three separate *ab initio* calculations required to evaluate the HOCO heat of formation. Averaging all four determinations yields our best estimate of -43.3 kcal mol⁻¹ to which we assign a conservative uncertainty of 2 kcal mol⁻¹. Similar calculations produce $\Delta H_f^{298\text{ K}}$ (*cis*-HOCO) = -41.4 kcal mol⁻¹, $\Delta H_f^{298\text{ K}}$ (TS2) = -17.9 kcal mol⁻¹, and $\Delta H_f^{298\text{ K}}$ (TS3) = -35.3 kcal mol⁻¹. Our $\Delta H_f^{298\text{ K}}$ (*trans*-HOCO) agrees well with the recently revised lower limit of -46.5 kcal mol⁻¹ reported by Ruscic and Litorja²¹ and suggests a further upward revision of 3 kcal mol⁻¹. The present result also implies that *trans*-HOCO lies 26.2 kcal mol⁻¹ below OH+CO, 1.4 kcal mol⁻¹ below H+CO₂, and 25.4 kcal mol⁻¹ below TS2. Thus, unimolecular decomposition of *trans*-HOCO requires less than 27 kcal mol⁻¹ to surmount both the OH+CO and H+CO₂ dissociation barriers.

Several immediate ramifications for the OH+CO reaction may be deduced from the revised energetics of the HCO₂ potential. Most important, the conclusions drawn from previous theoretical treatments of the reaction should be considered suspect until the effect of decreasing the HOCO well depth by 9 kcal mol⁻¹ can be thoroughly investigated. We estimate the effect that the shallower potential well has on the microcanonical rate constant for HOCO dissociation by

noting that $k(E)$ depends inversely on the density of states, $\rho(E)$,

$$k(E) = \frac{N(E)}{h\rho(E)}. \quad (1)$$

Evaluating the density of vibrational states $\rho(E_v)^{25}$ at the old and new HOCO well depths

$$\frac{k(26.2 \text{ kcal mol}^{-1})}{k(35.4 \text{ kcal mol}^{-1})} \cong \frac{\rho(35.4 \text{ kcal mol}^{-1})}{\rho(26.2 \text{ kcal mol}^{-1})} \quad (2)$$

we anticipate that the calculated rate constant for the revised thermochemistry is approximately a factor of 3 larger than the rate constant calculated from the old thermochemistry.¹⁹ The sparser density of states near the HOCO dissociation limit of the shallower potential should increase the importance of reactive scattering resonances to $k(E)$ in this energy region. This conclusion may be tested experimentally by obtaining rovibrational spectra of HOCO in the neighborhood of the dissociation threshold. The HOCO potential well determined by the present study requires only three quanta of the OH stretching vibration ($E_v \sim 30$ kcal mol⁻¹) to exceed the dissociation barriers into both the OH+CO and the H+CO₂ channels. Interesting tunneling dynamics may already exist for molecules possessing two quanta of OH stretching excitation. In fact, all HOCO excited vibrational states have energies above the H+CO₂ thermodynamic

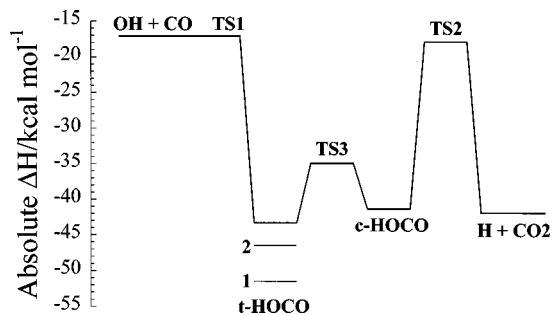


FIG. 1. A schematic diagram of the HCO₂ potential energy surface. The *ab initio* enthalpies calculated in the present work are shown as the connected lines. The experimental values for $\Delta H_f^{298\text{ K}}$ (*trans*-HOCO) from Refs. 19 and 21, labeled 1 and 2, respectively, are included for comparison.

TABLE II. Enthalpies (kcal mol⁻¹) on the HCO₂ potential relative to OH+CO.

	OH+CO	<i>t</i> -HOCO	TS3	<i>c</i> -HOCO	TS2	H+CO ₂
0 K						
CBS-QB3	0.0	-25.4	-17.3	-23.4	1.1	-25.0
G3	0.0	-24.3	-16.2	-22.4	0.0	-24.5
Expt ^a	0.0	-27.8				-24.3
298 K						
CBS-QB3	0.0	-27.0	-19.0	-24.9	-0.5	-25.4
G3	0.0	-25.8	-17.9	-23.9	-1.5	-24.9
Expt ^a	0.0	-29.4				-24.9

^aExperimental enthalpies taken from Refs. 18 and 21.

TABLE III. Calculated heats of formation for *trans*-HOCO, *cis*-HOCO, TS2, and TS3.^a

	ΔH_1	ΔH_{f1}	ΔH_2	ΔH_{f2}	
<i>trans</i>-HOCO					
0 K					
CBS-QB3	-25.4	-43.5	-0.4	-42.7	-45.8 Expt^b
G3	-24.3	-42.3	0.2	-42.1	-42.7 Average
298 K					
CBS-QB3	-27.0	-44.1	-1.5	-43.5	-46.5 Expt^b
G3	-25.8	-42.9	-0.9	-42.8	-43.3 Average
<i>cis</i>-HOCO					
0 K					
CBS-QB3	-23.4	-41.4	1.6	-40.7	
G3	-22.4	-40.4	2.1	-40.3	-40.7 Average
298 K					
CBS-QB3	-24.9	-42.0	0.5	-41.5	
G3	-23.9	-41.0	1.0	-41.0	-41.4 Average
TS2					
0 K					
CBS-QB3	1.1	-17.0	25.0	-17.3	
G3	0.0	-18.0	24.5	-17.8	-17.5 Average
298 K					
CBS-QB3	-0.5	-17.6	25.0	-17.0	
G3	-1.5	-18.6	23.4	-18.5	-17.9 Average
TS3					
0 K					
CBS-QB3	-17.3	-35.3	7.7	-34.6	
G3	-16.2	-34.2	8.3	-34.0	-34.6 Average
298 K					
CBS-QB3	-19.0	-36.1	6.5	-35.5	
G3	-17.9	-35.0	7.1	-34.9	-35.3 Average

^aExperimental enthalpies for OH, CO, H and CO₂ taken from Ref. 18. $\Delta H_1 = \Delta H_f^{ab, initio}(X) - \Delta H_f^{ab, initio}(\text{OH} + \text{CO})$; $\Delta H_{f1} = \Delta H_1 + \Delta H_f^{\text{expt}}(\text{OH} + \text{CO})$ where $\Delta H_f^{\text{expt}, 0 \text{ K}}(\text{OH} + \text{CO}) = -18.03 \text{ kcal mol}^{-1}$, $\Delta H_f^{\text{expt}, 298 \text{ K}}(\text{OH} + \text{CO}) = -17.10 \text{ kcal mol}^{-1}$; $\Delta H_2 = \Delta H_f^{ab, initio}(X) - \Delta H_f^{ab, initio}(\text{H} + \text{CO}_2)$; $\Delta H_{f2} = \Delta H_2 + \Delta H_f^{\text{expt}}(\text{H} + \text{CO}_2)$ where $\Delta H_f^{\text{expt}, 0 \text{ K}}(\text{H} + \text{CO}_2) = -42.33 \text{ kcal mol}^{-1}$, $\Delta H_f^{\text{expt}, 298 \text{ K}}(\text{H} + \text{CO}_2) = -41.95 \text{ kcal mol}^{-1}$.

^bReference 21.

threshold and may possibly dissociate via quantum tunneling. Clearly, a great deal remains to be learned about this well-studied system.

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