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Reaction of HO with CO: Tunneling Is Indeed Important

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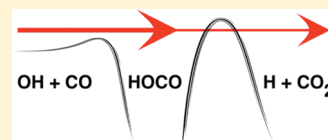
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Supporting Information

ABSTRACT: The potential energy surface and chemical kinetics for the reaction of HO with CO, which is an important process in both combustion and atmospheric chemistry, were computed using high-level *ab initio* quantum chemistry in conjunction with semiclassical transition state theory under the limiting cases of high and zero pressure. The reaction rate constants calculated from first principles agree extremely well with all available experimental data, which range in temperature over a domain that covers both combustion and terrestrial atmospheric chemistry. The role of quantum tunneling is confirmed to be extremely important, which supports recent work by Continetti and collaborators regarding the loss of hydrogen atoms from vibrationally excited states of HOCO. A sensitivity analysis has been carried out and serves as the basis for a plausible estimate of uncertainty in the calculations.

SECTION: Kinetics and Dynamics



The reaction of carbon monoxide with hydroxyl radicals ($\text{CO} + \text{OH}$) is quite important in both combustion and atmospheric chemistry;^{1,2} this reaction and the associated HOCO intermediate are also believed to be important in planetary science, especially with regards to the Martian atmosphere.³ Accordingly, it has been extensively studied by both experimental and theoretical work.^{1–16} Thermal rate constants measured for a wide range of temperatures and pressures show significant non-Arrhenius behavior and strong pressure dependence.^{1–7} Recently, dissociative photodetachment studies of the HOCO^- anion by Johnson et al.^{8,9} revealed that the dissociation of HOCO occurs below calculated barriers to the products $\text{H} + \text{CO}_2$, which implies that quantum mechanical tunneling plays an important role. Potential energy surfaces (PESs) have been constructed by a number of groups^{12–14} using high levels of theory. Thermal rate constants computed based on these PESs using the quasi-classical trajectory (QCT) technique¹⁴ agree well with the experimental data when the temperature is above 1000 K but are significantly underestimated below 1000 K, where the measured rate constant falls only very slowly with temperature. This defect may be attributed to the fact that tunneling corrections are neglected in the calculations. Very recently, Liu et al.¹⁵ have carried out a full-dimensional time-dependent wave packet study using the Lakin–Troya–Schatz–Harding (LTSH) PES; however, agreement between their high-quality theoretical results with both the QCT and experimental data is poor, which implicates a problem with the LTSH surface. An excellent review of previous work on this system has very recently been given by Guo.¹⁷

In this Letter, we have restudied the PES of the title reaction using the high-accuracy HEAT protocol^{18–20} and semiclassical transition state theory (SCTST).^{21–25} The latter has been used

to compute rate constants at the high- and zero-pressure limits using the high-quality potential energy surface reported here.

Computational Approach. *Ab Initio Calculations.* All stationary points including minima and transition structures on the lowest-lying doublet electronic PES were computed using the HEAT protocol (see Figure 1).^{18–20} This model chemistry

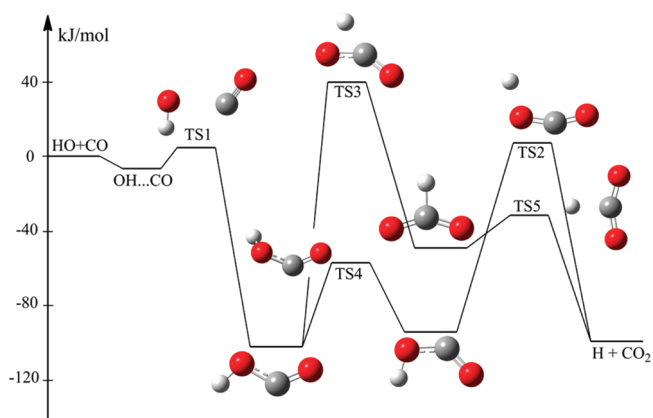


Figure 1. Most important reaction paths on the lowest-lying doublet electronic potential energy surface in the $\text{HO} + \text{CO}$ reaction, constructed using the HEAT protocol.

includes a treatment of electron correlation that includes quadruple excitations (the variant used here is HEAT-345Q¹⁹) and does not contain any empiricism apart from that associated with the basis set extrapolation techniques. In addition to the

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Table 1. Calculated Vibrational Adiabatic Relative Energies (kJ/mol) for Various Species in the HO + CO Reaction Using the HEAT Protocol^a

species	FCC/CBS ^b	G2M ^c	CBS-QB3 ^d	G3 ^d	HEAT
HO + CO	0.00	0.00	0.00	0.00	0.00
H + CO ₂	-102.88	-103.34	-104.60	-102.51	-103.29
PRC, OH-CO	-4.07	-7.53			-5.81
PRC, OH-OC	-1.22	-4.18			-0.22
<i>trans</i> -HOCO	-106.03	-100.00	-106.27	-101.67	-103.84
<i>cis</i> -HOCO	-99.02	-93.30	-97.91	-93.72	-97.49
H-CO ₂	-41.00	-37.66			-49.31
TS1	2.37	3.35			3.59
TS2	4.31	9.62	4.60		8.16
TS3	35.90	44.77			40.03
TS4	-71.84	-65.27	-72.38	-67.78	-69.62
TS5	-43.31	-39.33			-36.76

^aOther theoretical values are given for comparison. ^bYu et al.¹² ^cZhu et al.¹¹ ^dDuncan et al.¹⁰

vibrational zero-point energy, other small adjustments such as scalar relativistic correction, first-order spin-orbit coupling, and the diagonal Born-Oppenheimer correction are included. For an elaborated discussion of the HEAT protocol and the accuracy that has been obtained by this procedure for thermochemical parameters, the interested reader is referred to refs 18–20. For minima on the potential energy surface, HEAT provides relative energies that have proven to have an accuracy of better than 1 kJ/mol; for transition states where the single-reference approach is still adequate (as in the case here), a similar accuracy might be expected. Unlike the original papers, in this work, we use zero-point anharmonic vibration energies (ZPE) obtained with CCSD(T) (in the frozen core approximation) in combination with the atomic natural orbital (ANO) basis set of Almlöf and Taylor.²⁶ A truncated ANO basis set, here referred to as ANO1, with the truncation of 4s2p1d for the H atom and 4s3p2d1f was used for the non-hydrogen atoms to obtain the anharmonic force fields. The harmonic force fields were computed with the ANO2 basis set, which was contracted as 4s3p2d1f for the H atom and 5s4p3d2f1g for C and O atoms. Second-order vibrational perturbation theory (VPT2)²⁷ was then used to compute the zero-point energy. The CFOUR program package²⁸ was used for all calculations.

Chemical Kinetics Calculations. To compute thermal rate constants as functions of both temperature and pressure (i.e., fall-off curve), one must use the master equation technique;²⁹ such a work is in progress and will be reported separately.³⁰ In this Letter, we focus on the high- and zero-pressure limits, which are both relevant to this particular reaction system and straightforward to compute. Therefore, the complicated effects of energy transfer by collisions with a third body are neglected. Analytical solutions of the two-dimensional master equation (i.e., depending on both the energy and overall rotation) for thermal rate constants under these two extremes for a reaction scheme as shown in Figure 1 are given by^{5,31–33}

$$k_{p=0}(T) = \frac{1}{h} \times \frac{Q_{\text{trans,elec}}^{\ddagger}}{Q_{\text{HO}}Q_{\text{CO}}} \times \sum_{J=0}^{+\infty} (2J+1) \int_0^{+\infty} \frac{G_1^{\ddagger}(E, J) G_{23}^{\ddagger}(E, J)}{G_1^{\ddagger}(E, J) + G_{23}^{\ddagger}(E, J)} \exp\left(-\frac{E}{k_{\text{B}}T}\right) dE \quad (1)$$

with $G_{23}^{\ddagger}(E, J) = G_2^{\ddagger}(E, J) + G_3^{\ddagger}(E, J)$

$$k_{p=\infty}(T) = \frac{1}{h} \times \frac{Q_{\text{trans,elec}}^{\ddagger}}{Q_{\text{HO}}Q_{\text{CO}}} \times \sum_{J=0}^{+\infty} (2J+1) \int_0^{+\infty} G_1^{\ddagger}(E, J) \exp\left(-\frac{E}{k_{\text{B}}T}\right) dE \quad (2a)$$

or

$$k_{p=\infty}(T) = \frac{k_{\text{B}}T}{h} \times \frac{Q_{\text{TS1}}^{\ddagger}}{Q_{\text{HO}}Q_{\text{CO}}} \times \exp\left(-\frac{\Delta E_{\text{TS1}}^{\ddagger}}{k_{\text{B}}T}\right) \quad (2b)$$

where h is Planck's constant, k_{B} is Boltzmann's constant, and Q_{HO} , Q_{CO} , and $Q_{\text{TS1}}^{\ddagger}$ are the total partition functions of HO, CO, and TS1, respectively. The electronic partition function of HO is given by $Q_{\text{HO}}^{\text{elec}} = 2 + 2 \exp(-139 \text{ cm}^{-1}/k_{\text{B}}T)$. $Q_{\text{trans,elec}}^{\ddagger}$ is a product of translational and electronic partition functions corresponding to the transition structure. $G_1^{\ddagger}(E, J)$, $G_2^{\ddagger}(E, J)$, and $G_3^{\ddagger}(E, J)$ are the rovibrational cumulative reaction probability (CRP) at each pair of (E, J) for TS1, TS2, and TS3, respectively. In this work, vibration and rotation are assumed to be separable; therefore, $G(E, J)$ can be computed by convolution and is expressed as

$$G(E, J) = \int_0^E G_{\text{vib}}(E - E_{\text{rot}}) \rho_{\text{rot}}(E_{\text{rot}}) dE_{\text{rot}} \quad (3)$$

Here, the vibrational CRP, $G_{\text{vib}}(E)$, is calculated using SCTST,²⁴ which naturally includes fully coupled vibrations and multidimensional tunneling; rotational energy levels of a rigid symmetric top molecule are used for the transition states, given by $E_{\text{rot}} = \bar{B}J(J+1) + (A - \bar{B})K^2$, with $\bar{B} = (B \times C)^{1/2}$ and $-J \leq K \leq J$. Both the CRP and the rotational density of states are obtained by explicit state counting, using an energy bin of 1 cm^{-1} , a maximum J of 200, and a ceiling energy of $5 \times 10^4 \text{ cm}^{-1}$ relative to the initial reactants. The latter two are chosen to be sufficiently high to ensure that all of reaction rates computed in the temperature range from 50 to 2500 K are converged. Equations 1 and 2a are computed by simple summation using step sizes of 1 cm^{-1} and unity for E and J , respectively. We have double-checked the results by comparing $k_{p=\infty}(T)$ calculated using eq 2a with $k(T)$ calculated for the $\text{HO} + \text{CO} \rightarrow \text{TS1} \rightarrow \text{HOCO}$ step using TST, eq 2b. The accuracy of numerical integrals evaluated for eqs 1 and 2a is found to be better than 1%.

Potential Energy Surface. The lowest-lying doublet electronic potential energy surface for the reaction of HO with CO has been studied theoretically by a number of groups^{10–14} but has previously been calculated at lower levels of theory. Briefly, classical relative energies (i.e., without ZPE corrections) calculated by Yu et al.¹² and Li et al.¹⁴ are in good agreement with our values, while the MRCI/CASSCF values reported by Song et al.³⁴ are somewhat further from the present set of values (see Table S1 in the Supporting Information). When comparing vibrationally adiabatic relative energies (i.e., with ZPE corrections), the difference between HEAT-345Q and the Yu et al. results is found to be as large as 5 kJ/mol (see Table 1). This is partly due to the fact that anharmonicity was ignored in the study of Yu et al. Finally, the differences between composite methods^{10,11} (i.e., G2M, G3, and CBS-QB3) and HEAT-345Q are found to be about 5 kJ/mol.

Figure 1 shows most important reaction processes, which can be briefly summarized as follows. The reaction of HO with CO starts with the formation of two hydrogen-bonded prereactive complexes (PRCs), OH–CO and OH–OC lying –5.8 and –0.2 kJ/mol below the initial reactants. Both PRCs have a $C_{\infty v}$ symmetry and a $^2\Pi$ electronic state. The PRC OH–OC has a very small binding energy and appears not to play any role in the reaction mechanism. The PRC OH–CO when formed can either dissociate back to the initial reactants or isomerize via TS1 to form *trans*-HOCO. The former step occurs more rapidly than the latter; therefore, the microcanonical equilibrium $\text{HO} + \text{CO} \rightleftharpoons \text{OH–CO}$ is assumed to be quickly established before OH–CO converts to *trans*-HOCO. It is worth noting that we have located another stationary point leading to *cis*-HOCO, but this conformer was found to be a second-order saddle point that connects two equivalent forms on the torsional potential surface (see Figure S1, Supporting Information). This finding is consistent with the previous work of Zhu et al.¹¹ but not with the others.^{12,14} For chemical kinetics calculations, we have treated the torsional motion of the H-atom around the O–C axis in TS1 as a separable one-dimensional hindered internal rotor. Therefore, the *cis* configuration of TS1 is also included implicitly in the kinetics calculations. There are three distinct reaction pathways from vibrationally excited *trans*-HOCO, which is formed with an internal energy of 103.8 kJ/mol. First, *trans*-HOCO can rapidly isomerize to *cis*-HOCO via the low-lying TS4, followed by hydrogen elimination via TS2 to produce $\text{H} + \text{CO}_2$. Second, from *trans*-HOCO there is another pathway indirectly leading to products via $\text{TS3} \rightarrow \text{H–CO}_2 \rightarrow \text{TSS}$, but this step needs to overcome a significantly higher barrier of 143.9 kJ/mol compared to 112.0 kJ/mol via TS2. Therefore, this reaction path might play some role at high temperatures only. It should be mentioned that H–CO_2 formed from *trans*-HOCO via TS3 would have an internal energy of more than 49 kJ/mol. Therefore, it will decompose promptly to the products $\text{H} + \text{CO}_2$ via TSS with a low barrier of ~12 kJ/mol. It should also be noted that the C_{2v} intermediate involved in this latter pathway is a well-known example where the Born–Oppenheimer approximation does not work particularly well;³⁵ therefore, the dynamics of this pathway would be very difficult to treat theoretically. Finally, nascent *trans*-HOCO can also redissociate to the initial reactants via TS1. This step faces the lowest barrier of 107.4 kJ/mol.

In summary, under collision-free conditions, the reaction rate constants and the yield of the products $\text{H} + \text{CO}_2$ from the $\text{HO} + \text{CO}$ reaction depend on the competition of three reactive

fluxes (i.e., cumulative reaction probabilities) via TS1, TS2, and TS3. While the reactive flux via TS1 is energetically favorable and therefore strongly preferred from the perspective of classical mechanics, the other two via TS2 and TS3 may be facilitated by quantum tunneling effects. The importance of tunneling via the pathway involving TS2 has recently been supported by the work of Johnson and Continetti. This competition is formulated in eq 1, and results from the chemical kinetics analysis will be given in the next section.

Reaction Rate Constants. Thermal rate constants as a function of temperature at the zero- and high-*P* limits were computed using eqs 1 and 2a and are displayed in Figure 2. Experimental

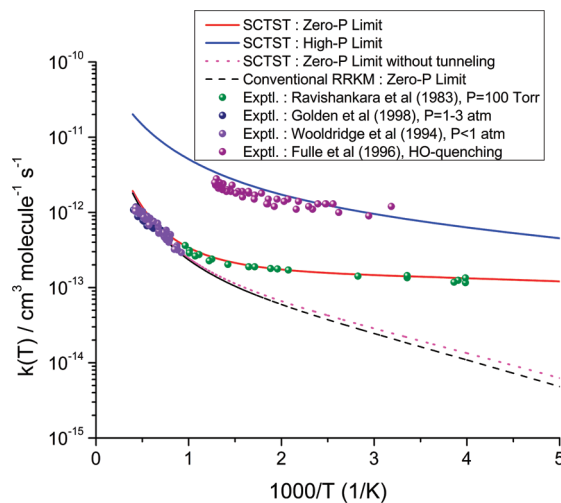


Figure 2. Calculated thermal rate constants as a function of temperature at the zero- and high-pressure limits for the $\text{HO} + \text{CO}$ reaction. Experimental data are included for the purpose of comparison.

data are included for comparison, while other theoretical results (see ref 14) are already mentioned above and are not shown here. As mentioned above, the torsional motion of the H atom around the O–C axis in TS1 is assumed to be separable from the other vibrations and was treated as a separable one-dimensional hindered internal rotor. A vector of eigenvalues was computed by solving the Schrodinger equation for the hindered internal rotor, in which the change in the moment of inertia as a function of torsional angle is taken into account (see Figure S2, Supporting Information). The direct-count method was then used to compute the rotational density of states,²⁹ which were subsequently convoluted with the other vibrational sum of states. Figure 2 shows that at the zero-*P* limit, our thermal rate constants are in line with low-pressure experiments for the temperature range from 250 to 1500 K and just slightly higher than the experiments at higher temperatures. It is significant that the calculations reproduce the rate constant very well at lower temperature, where previous efforts have fared much worse. To study the role of tunneling, the simulation was rerun with the tunneling contribution turned off either by using the same SCTST approach but setting all constants α_{IF} , α_{FF} , and ω_{F} , which lead to tunneling, equal to zero or by using RRKM theory, with the calculated harmonic frequencies. The calculated thermal rate constants without tunneling are also plotted in Figure 2. The small differences in the thermal SCTST rate constants computed without tunneling versus rate constants computed from conventional RRKM theory are

mainly due to the differences in ZPEs used in the two types of calculations and partly due to the anharmonic intermode couplings included in SCTST approach but neglected in the RRKM calculations.

It is clear that tunneling effects are very important below 1000 K and increase markedly at the lower temperatures relevant to the atmosphere. At room temperature, the tunneling enhancement is a factor of ~ 6.5 , implying that more than 85% of the reactive flux proceeds to products by tunneling through the barrier. As one might suppose, theoretical methods^{12–14} that do not incorporate tunneling significantly underestimate the experimental data at $T < 1000$ K, although they all employed high-level quantum chemical surfaces that are in good agreement with the present PES. The reason for their poor performance is because they used quasi-classical trajectory calculations, which neglect quantum mechanical tunneling.

Our thermal SCTST rate constants calculated at the high- P limit are also in good agreement with the experimental rate constants measured by Fulle et al.⁵ for quenching of vibrationally excited OH. If it is assumed that the quenching occurs exclusively by chemical reaction, Fulle's rate constants should correspond to the high-pressure reaction rate. At around room temperature, the agreement is excellent, but the agreement is not as good at higher temperatures. It is possible that the vibrational quenching rate constants do not correspond exactly to the high-pressure limit. It is also possible that pressure effects are still important, and it will be interesting to see how good the master equation simulations are.

The calculated SCTST rate constants sensitively depend on several parameters, including barrier heights, rovibrational parameters, and anharmonic constants. Of these, the uncertainty in the barrier height is unquestionably paramount. Given that the calculated barriers using HEAT are expected to have errors of up to of ~ 1 kJ/mol, we shifted the energies of TS1 or TS2 in Figure 1 by this amount in order to carry out a simple sensitivity analysis. The thermal reaction rates calculated with and without the change in energy of TS1 or TS2 are plotted in Figure 3 (also see Figure S3, Supporting Information). It is clear that the effects of TS1 on the calculated rates are more pronounced than TS2, especially at low temperatures. At 200 K, a shift of TS1 by 1 kJ/mol alters

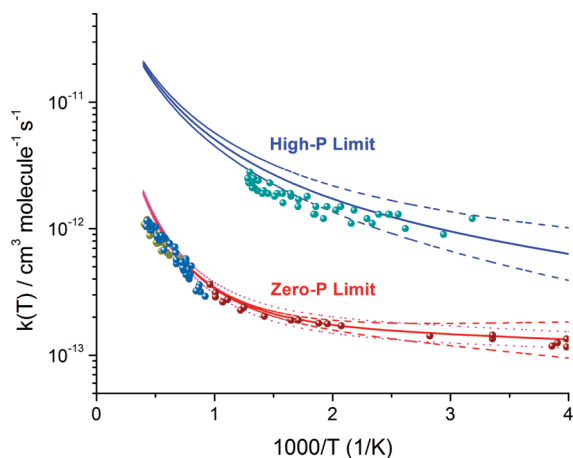


Figure 3. Calculated thermal rate constants as a function of temperature and a function of the position of TS1 or TS2 for the HO + CO reaction. (Solid line) Ab initio results; (dash lines) shift TS1 by ± 1 kJ/mol; (dot lines) shift TS2 by ± 1 kJ/mol.

the reaction rate by $<60\%$, but it is only about 15% when changing TS2 by the same amount. However, the sensitivity of the results with respect to the TS1 barrier height is reduced at higher temperature. In contrast, the computed reaction rates are relatively insensitive to change in the energy of TS2. Overall, most of the experimental values fall within the lower and upper limits of the theoretical reaction rate constants when the energies are varied as described, which suggests that the parameters calculated in this work are very accurate.

The potential energy surface of the reaction of OH with CO was reinvestigated using the HEAT protocol, followed by chemical kinetics calculations for thermal reaction rate constants as a function of temperature at the zero- and high- P limits using SCTST. Our purely ab initio thermal rate constants are in excellent agreement with all of the low-pressure experimental data from 250 to 2000 K. The theoretical high-pressure rate constants are a little higher than those from experiments, which were obtained at finite pressures. This is the first time that a theoretical analysis has characterized the rate of this fundamentally important reaction so accurately. Highly significant is the finding that quantum mechanical tunneling appears to be responsible for more than 80% of the rate at atmospheric temperatures. Thus, we concur with Johnson and Continetti that quantum tunneling through TS2 is a vital part of the dynamics in this interesting chemical system.

■ ASSOCIATED CONTENT

● Supporting Information

Optimized geometries, rovibrational parameters, anharmonic constants, and energies for various species in the HO + CO reaction are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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