Accurate Rate Constants for the Forward and Reverse H + CO ↔ HCO Reactions at the High-Pressure Limit

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ABSTRACT: The forward and reverse H + CO ↔ HCO reactions are important for combustion chemistry and have been studied from a wide variety of theoretical and experimental techniques. However, most of the chemical kinetic investigations concerning these processes are focused on low pressures or fall-off regions. Hence, a high-level electronic structure treatment was employed here in order to provide accurate rate constant values for these reactions at the high-pressure limit along temperatures from 50 to 4000 K. In relative terms, the variational effects on rate constants are shown to be almost as important at high temperatures as quantum tunneling corrections at the lowest temperatures investigated. The activation energies fitted by using modified and traditional Arrhenius’ equations for the forward rate constants from 298 to 2000 K are, respectively, equal to 2.64 and 3.89 kcal mol⁻¹, while similar fittings provided, respectively, 1.96 and 3.22 kcal mol⁻¹, considering now forward rate constants from a temperature range of 298–373 K. This last activation energy determination (3.22 kcal mol⁻¹) is in better agreement with the commonly referenced experimental value of 2.0 ± 0.4 kcal mol⁻¹, also obtained from traditional fittings in the range 298–373 K, than the value attained from a broader temperature range fitting (3.89 kcal mol⁻¹). However, some additional care must be considered along these comparisons once the experimental reaction rate measurements have been done for the trimolecular H + CO + M → HCO + M reaction instead. Anyway, the usage of appropriate temperature ranges is fundamental for reliable activation energy comparisons, although the remaining deviation between theory and experiment is still large and is possibly caused by the different pressure regimes assessed in each case. Finally, we roughly estimated that the high-pressure limit for the HCO decomposition into H and CO can be achieved along temperatures ranging from ~246 and ~255 K downward, respectively, at pressures of 1.1 and 9.6 atm, although further experiments should be carried out in order to improve these estimates. On the other hand, pressures larger than 9.8 × 10⁵ atm are required for the aforementioned dissociation reaction to attain the high-pressure limit at 700 K. Therefore, the rate constants determined here are probably applicable in combustion studies at lower temperatures.

1. INTRODUCTION

The formyl radical, HCO, is an important intermediate in combustion chemistry commonly produced from flash photolysis of acetaldehyde¹ in ethylene flames² or even in other hydrocarbon flames involving the CH + O → HCO + e⁻ and CH + O → CO* + H processes.³ Furthermore, the HCO production from the forward reaction

\[ H^*(S_{1/2}) + CO(X^1Σ^+) \rightarrow HCO(X^2A) \]  

was observed experimentally and numerically by Burke et al.⁴ as being responsible for the consumption of up to 8.4% of hydrogen atoms produced during the mass burning rate study in H₂/CO/O₂/diluent flames with temperatures and pressures reaching 1800 K and 25 atm, respectively. In turn, Li et al.⁵ mention HCO + O₂ and the reverse reaction (1) as the principal paths for CO production during high-temperature combustion of hydrocarbons. Besides, taking into consideration the main oxidation path of some small hydrocarbons (such as in the CH₄ → CH₃ → H₂CO → HCO → CO → CO₂ sequential mechanism), Friedrichs et al.⁶ point out HCO + H, HCO + OH and the reverse reaction (1) as routes to generate carbon monoxide, whereas an investigation accomplished by Westbrook et al.⁷ in turbulent flow reactors confirms this last reaction as being the major pathway for CO formation from the CH₄ oxidation. Beyond its relevance for CO production, combustion kinetic models also showed that the incorporation of prompt HCO dissociation into the simulations is able to influence flame speeds of hydrocarbon and oxygenated molecules because of the additional source of hydrogen atoms produced by this chemical process.⁸

An experimental determination of Arrhenius’ activation energy for the H + CO + M → HCO + M reaction done by Wang et al.⁹ furnished 2.0 ± 0.4 kcal mol⁻¹ from a fitting
performed with rate constants measured between 298 and 373 K. Alternatively, Arai et al. estimated rate constants for the HCO production from H + CO at atmospheric pressures and temperatures from 345 to 449 K, providing apparent Arrhenius’ activation energy of 4.1 kcal mol⁻¹. Taking into account that Arrhenius’ activation energies and barrier heights are conceptually distinct quantities, the value of Wang et al. has been erroneously used as a reference in discussions concerning theoretical barrier height results obtained for reaction 1. This inappropriate comparison provides theoretical barrier heights always larger than the experimental ‘reference’ value mentioned in these studies, which would require additional experiments in order to elucidate the reason for this persisting discrepancy. Anyway, accurate activation energy values and the investigation of their dependence with temperature and pressure are certainly fundamental for the understanding of ignition processes and also to obtain reliable combustion chemistry models.

Despite the considerable importance of HCO dissociation into H and CO for combustion chemistry, most of theoretical and experimental studies found in the literature are performed at low and moderate pressures, providing only second-order rate constants for the above decomposition process (e.g., refs 6,13,14,17). Even at pressures nearby ~100 atm, Krasnoperov et al. also measured second-order rate constants for the HCO decomposition into H and CO, and their experiments attest a pressure dependence of such constants between 498 and 769 K. Hippler et al. also investigated the rate constants for the HCO dissociation between temperatures of 590 and 800 K and pressures ranging from 1 to 140 bar, mentioning that the values obtained at 100 bar are “more than one order below the high-pressure limit”.

In terms of theoretical studies, Machado and Bauerfeld calculated high-pressure limit rate constants for the HCO → H + CO process as well as for other five elementary reactions in order to apply a chemical model for the H₂CO + OH reaction. However, they only showed the parameters resulting from traditional Arrhenius’ equation fitted between 200 and 2200 K. High-pressure limit rate constant values for the H + CO → HCO reaction are presented by Andersson et al., but their data are restricted to a temperature range from 5 to 180 K. Other theoretical investigations concerning the forward and reverse H + CO ↔ HCO reactions can also be mentioned, which explore sundry properties from diverse methodologies (e.g., refs 11,12,17,18). Finally, Timonen et al. and Wagner and Bowman estimated theoretically that the high-pressure limit of the H + CO reaction should be reached somewhere between 100 and ~10,000 atm at room temperature. However, these authors also comment that additional experiments are required to confirm this high-pressure limit interval.

We demonstrated in a recent theoretical study regarding the chemical mechanism for the reaction between CH and CO₂ that H and CO are the main products formed at temperatures larger than 300 K, whereas HCO and CO are preferential from 300 K downward. Hence, the rate constants for reaction 1 were also determined in this previous investigation. However, the main goal of the present study is to employ a more advanced electronic structure treatment than the one used in the reference mentioned above in order to provide the most accurate estimates for rate constants for the forward and reverse H + CO ↔ HCO reactions at the high-pressure limit. In addition, the variational and quantum tunneling effects on such rate constants are evaluated and discussed in details. Finally, we show resulting Arrhenius’ parameters obtained for such pressure regime at two different temperature ranges, reinforcing the importance of this factor for proper activation energy comparisons.

2. RESULTS AND DISCUSSION

According to calculations performed by means of the unrestricted coupled cluster treatment with single and double excitations (CCSD) along with the augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ), the H + CO ↔ HCO reaction proceeds through a single elementary step involving a very weak precomplex, and the stationary point structures encountered are illustrated in Figure 1.

The optimized geometries are described in Table S1. Thus, one can notice an excellent agreement between CCSD/aug-cc-pVTZ geometries and the available experimental data for reactants and product,

whereas the deviation for the bond angle of HCO is 0.4%. Our calculations for HCO provided equilibrium parameters of 1.177 and 1.176 Å for H–C and C–O bond lengths, respectively, along with 129.6° for the H–C–O angle, which are in good agreement with the data obtained by Song et al. from UCCSD(T)/CBS potential energy surfaces with basis set superposition error corrections (1.119, 1.175 Å, and 124.6°) or even from MRCI+Q/cc-pCVSZ-DK calculations done by Peters et al. (1.116, 1.176 Å, and 124.6°) (see Table S1). In turn, this table also shows that the geometrical parameters found in this study for the TSRP structure (1.846, 1.134 Å, and 117.1°) in the same order mentioned before agree once more with these results achieved by Song et al. (1.865, 1.133 Å, and 116.0°) and by Peters et al. (1.847, 1.133 Å, and 117.2°). In addition, Woon calculated similar values for TSRP at the CCSD(T)/cc-pVQZ level (1.836, 1.136 Å, and 117.0°). The T₁ diagnostic for all structures found here is ≤0.022, which is consistent with the values recommended by Lee and Taylor and Rienstra-Kiracofe et al. (see Table S1), justifying the good agreement seen for the TSPR geometry from MRCI+Q and CCSD calculations and, therefore, reinforcing the reliability of the single-reference CCSD(T) treatment for investigating the thermochemical and kinetic properties of the H + CO ↔ HCO reaction.

In accordance, scaled vibrational frequencies obtained here for CO and HCO (see Table S2) deviate by, at most, 5.4% with respect to experiments. As one can also observe in this table, our scaled fundamental vibrational frequency results for HCO are also in fair agreement with other theoretical data by Song et al. and Peters et al. There is also some debate in the literature regarding the existence of a precomplex in the studied reaction, which was
characterized here. However, the MRCI+Q/aug-cc-pVQZ calculations done by Peters et al.\textsuperscript{11} agree with our study, indicating the possible formation of a very weak precomplex. The CO and CH bond lengths found by these authors are 1.134 and 3.516 Å, respectively, with a HCO bond angle of 102.2°. Our values for CO and CH distances for the prebarrier complex (PrC) are 1.129 and 3.589 Å, respectively, while the HCO angle is 98.7°.

Figure 2 exhibits electronic energies relative to reactants (H + CO) obtained here from a combined treatment, labeled hereafter CCSD(T)/CBS//CCSD/aug-cc-pVTZ. Thus, the forward and reverse reactions in the study present barrier heights of 3.21 and 22.52 kcal mol\textsuperscript{-1}, respectively, which are in great accordance with the values of 3.17 and 22.68 kcal mol\textsuperscript{-1} (forward reaction exoergic by 19.51 kcal mol\textsuperscript{-1}) achieved from the W1 method by Zhao et al.\textsuperscript{22} Our work is also in excellent agreement with the UCCSD(T)/CBS results from Song et al.,\textsuperscript{27} whose obtained barrier heights of 3.25 and 22.51 kcal mol\textsuperscript{-1} for the forward and reverse H + CO ↔ HCO reactions, respectively, whereas the value of 19.26 kcal mol\textsuperscript{-1} was found for the electronic energy change of this reaction. The PrC is only 0.10 kcal mol\textsuperscript{-1} more stable than the reactants according to electronic energies obtained in this work (see Figure 2). By comparison, Peters et al.\textsuperscript{11} found a stabilization energy of 0.07 kcal mol\textsuperscript{-1} for this molecular complex according to MRCI+Q/aug-cc-pVQZ calculations. Thus, although theoretical calculations point out the existence of a very weak precomplex along the reaction in the study, this structure may dissociate spontaneously because of molecular vibrations (notice the slightly positive value associated with PrC, as shown in Figure 2, as \( \varepsilon_0 \) corrections are taken into account, 0.01 kcal mol\textsuperscript{-1}). Anyway, this possible dissociation of PrC is not worth of concern for our study because insignificant deviations are expected in rate constants whether this molecular structure is or not considered in the calculations.

In turn, the forward reaction becomes less exoergic by adding zero-point corrections to electronic energies, \(-14.4\text{ kcal mol}^{-1}\) (see Figure 2), which is in great agreement with the experimental enthalpy change of \(-14.540 ± 0.023\text{ kcal mol}^{-1}\) at 0 K presented by Rusnic and Bross.\textsuperscript{31} Beyond this, the aforementioned value obtained here is also consistent with \(-14.1\text{ kcal mol}^{-1}\), provided by Chase\textsuperscript{32} as well as with other two alternative experimental results mentioned by Peters et al.,\textsuperscript{11} \(-14.3\) and \(-13.9\text{ kcal mol}^{-1}\).

Figure 3 displays enthalpies and Gibbs energies relative to reactants for the H + CO ↔ HCO reaction at 50, 300, 1000, 2500, and 4000 K. Complementarily, one can find in Tables S3 and S4 the numerical values of these thermochemical properties at these and other temperatures along the range from 50 to 4000 K. At first, the CCSD(T)/CBS//CCSD/aug-cc-pVTZ calculations demonstrate that the HCO formation from H + CO is an exoergic process at all temperatures analyzed (ranging from \(-14.60\) to \(-18.72\text{ kcal mol}^{-1}\) at 50 and 4000 K, respectively). Furthermore, all enthalpy change (\( \Delta H \)) results obtained here along 100–4000 K (see Table S3) are in great accordance with experimental data furnished by Chase,\textsuperscript{32} presenting a maximum discrepancy of only 0.42 kcal mol\textsuperscript{-1}. As is observed in Table S3, this discrepancy becomes larger, 0.6 kcal mol\textsuperscript{-1}, when experimental values are compared with enthalpy energy changes obtained in our previous study from the ROCCSD(T)/CBS//UCCSD/cc-pVDZ treatment.\textsuperscript{23} Consistently, the enthalpy change attained in this study for the HCO decomposition at 300 K, 15.58 kcal mol\textsuperscript{-1}, also agrees with other three experimental values, 15.4, 15.69 ± 0.19, and 15.703 ± 0.023 kcal mol\textsuperscript{-1}, which were measured at 298 K and presented by Baulch et al.,\textsuperscript{33} Chuang et al.,\textsuperscript{34} and Rusnic and Bross,\textsuperscript{31} respectively.

Relative Gibbs energy results, as presented in Table S4, indicate a change in the spontaneity direction for the H + CO → HCO reaction around 700 K, so that it is nonspontaneous at larger temperatures. Beyond this, all Gibbs energy changes (\( \Delta G \)) from 100 to 4000 K (see Table S4) are once more consistent with the experimental data provided by Chase\textsuperscript{32} along this same temperature range, with the largest deviation of only 0.28 kcal mol\textsuperscript{-1}, whereas the previous ROCCSD(T)/CBS//UCCSD/cc-pVDZ results provide a larger deviation of 0.6 kcal mol\textsuperscript{-1}\textsuperscript{23} as observed in Table S4. In accordance, the Gibbs energy change obtained in this study at 300 K is only 0.2 kcal
Table 1. Forward (in cm³ particle⁻¹ s⁻¹), $k_f$, and Reverse (in s⁻¹), $k_r$, Rate Constants Encountered for the H + CO ↔ HCO Reactions, as Calculated at the CCSD(T)/CBS//CCSD/aug-cc-pVTZ Level and Different Temperatures (in K), $T$

| $T$ (K) | $k_f$ | TST | ICVT | TST/W | ICVT/SCT | Dev* |
|---------|-------|-----|------|-------|----------|------|
| 50      | $7.30 \times 10^{-27}$ | $6.09 \times 10^{-27}$ | $1.68 \times 10^{-25}$ | $9.86 \times 10^{-27}$ | 100.0 |
| 100     | $7.89 \times 10^{-19}$ | $7.13 \times 10^{-19}$ | $5.13 \times 10^{-18}$ | $3.73 \times 10^{-16}$ | 99.9 |
| 200     | $8.72 \times 10^{-15}$ | $8.07 \times 10^{-15}$ | $2.07 \times 10^{-14}$ | $3.55 \times 10^{-14}$ | 77.3 |
| 300     | $2.12 \times 10^{-13}$ | $1.95 \times 10^{-13}$ | $3.42 \times 10^{-13}$ | $3.60 \times 10^{-13}$ | 45.8 |
| 500     | $3.16 \times 10^{-12}$ | $2.82 \times 10^{-12}$ | $3.86 \times 10^{-12}$ | $3.48 \times 10^{-12}$ | 19.1 |
| 700     | $1.12 \times 10^{-11}$ | $9.66 \times 10^{-12}$ | $1.24 \times 10^{-11}$ | $1.07 \times 10^{-11}$ | 10.1 |
| 1000    | $3.19 \times 10^{-11}$ | $2.63 \times 10^{-11}$ | $3.36 \times 10^{-11}$ | $2.78 \times 10^{-11}$ | 5.1 |
| 1500    | $8.18 \times 10^{-11}$ | $6.33 \times 10^{-11}$ | $8.38 \times 10^{-11}$ | $6.48 \times 10^{-11}$ | 2.3 |
| 2000    | $1.43 \times 10^{-10}$ | $1.04 \times 10^{-10}$ | $1.45 \times 10^{-10}$ | $1.06 \times 10^{-10}$ | 1.3 |
| 2500    | $2.09 \times 10^{-10}$ | $1.46 \times 10^{-10}$ | $2.11 \times 10^{-10}$ | $1.47 \times 10^{-10}$ | 0.8 |
| 3000    | $2.80 \times 10^{-10}$ | $1.87 \times 10^{-10}$ | $2.82 \times 10^{-10}$ | $1.88 \times 10^{-10}$ | 0.6 |
| 3500    | $3.53 \times 10^{-10}$ | $2.27 \times 10^{-10}$ | $3.54 \times 10^{-10}$ | $2.28 \times 10^{-10}$ | 0.4 |
| 4000    | $4.27 \times 10^{-10}$ | $2.65 \times 10^{-10}$ | $4.28 \times 10^{-10}$ | $2.66 \times 10^{-10}$ | 0.3 |

| $T$ (K) | $k_r$ | TST | ICVT | TST/W | ICVT/SCT | Dev* |
|---------|-------|-----|------|-------|----------|------|
| 50      | $1.82 \times 10^{-67}$ | $1.52 \times 10^{-67}$ | $4.19 \times 10^{-66}$ | $2.46 \times 10^{-67}$ | 100.0 |
| 100     | $1.19 \times 10^{-27}$ | $1.07 \times 10^{-27}$ | $7.73 \times 10^{-27}$ | $1.10 \times 10^{-24}$ | 99.9 |
| 200     | $1.44 \times 10^{-7}$ | $1.34 \times 10^{-7}$ | $3.43 \times 10^{-7}$ | $5.88 \times 10^{-7}$ | 77.3 |
| 300     | $9.26 \times 10^{-1}$ | $8.51 \times 10^{-1}$ | $1.49 \times 10^{0}$ | $1.57 \times 10^{0}$ | 45.8 |
| 500     | $3.46 \times 10^{1}$ | $3.09 \times 10^{1}$ | $4.23 \times 10^{1}$ | $3.82 \times 10^{1}$ | 19.1 |
| 700     | $9.95 \times 10^{7}$ | $8.60 \times 10^{6}$ | $1.11 \times 10^{8}$ | $9.57 \times 10^{7}$ | 10.1 |
| 1000    | $7.75 \times 10^{9}$ | $6.41 \times 10^{8}$ | $8.18 \times 10^{9}$ | $6.75 \times 10^{8}$ | 5.1 |
| 1500    | $2.52 \times 10^{11}$ | $1.95 \times 10^{11}$ | $2.58 \times 10^{11}$ | $2.00 \times 10^{11}$ | 2.3 |
| 2000    | $1.49 \times 10^{12}$ | $1.09 \times 10^{12}$ | $1.51 \times 10^{12}$ | $1.11 \times 10^{12}$ | 1.3 |
| 2500    | $4.39 \times 10^{12}$ | $3.07 \times 10^{12}$ | $4.43 \times 10^{12}$ | $3.09 \times 10^{12}$ | 0.8 |
| 3000    | $9.09 \times 10^{12}$ | $6.07 \times 10^{12}$ | $9.14 \times 10^{12}$ | $6.11 \times 10^{12}$ | 0.6 |
| 3500    | $1.53 \times 10^{13}$ | $9.84 \times 10^{12}$ | $1.54 \times 10^{13}$ | $9.89 \times 10^{12}$ | 0.4 |
| 4000    | $2.27 \times 10^{13}$ | $1.41 \times 10^{13}$ | $2.28 \times 10^{13}$ | $1.41 \times 10^{13}$ | 0.3 |

*Absolute deviations (in %) calculated from ICVT rate constants with respect to the ICVT/SCT ones.

As expected, the quantum tunneling effects are quite large at the lowest temperatures considered (see the last column of Table 1) so that forward and reverse ICVT/SCT rate constants are $1.61 \times 10^{10}$ and 1028 times larger than those values calculated by the ICVT treatment at 50 and 100 K, respectively. However, such effects become much less important as the temperature rises, once deviations between ICVT/SCT and ICVT rate constants decay from 77.3 (at 200 K) to 0.3% (at 4000 K). Andersson et al. also studied the influence of quantum tunneling effects on the rate constants of the H + CO → HCO reaction along $5\rightarrow180$ K. According to these authors, the ratio between rate constants with and without quantum tunneling corrections at 50 and 100 K are $1.34 \times 10^2$ and 540, respectively, which are smaller than our estimates.

Unsurprisingly, $k_f$ and $k_r$ values from the ICVT methodology are always smaller than those obtained from the TST treatment at each temperature, which is explained by variational effects on rate constants. In this sense, Table 2 displays the contribution of such effects from the ICVT results with respect to rate constants encountered by means of traditional TST. Thus, one can observe an increase of only 0.02 kcal mol⁻¹ in the Gibbs energy of activation because of variational effects at 50 K. This maximum Gibbs energy structure is located between TSRP and HCO along the reaction coordinate, more specifically at 0.03 Å from TSRP. Although this energy difference seems insignificant, it is enough to reduce the ICVT rate constant by 19.8% when compared to the TST value at 50 K. The relative contributions of variational effects to rate constants between 100 and 700 K are smaller, ranging from 8.1 to 15.7%. However, such effects become increasingly more important from 1000 K upward. For instance, the deviation between ICVT and TST rate constants...
achieved in this study, regarding the high-pressure limit, and experimental values measured by Hippler et al. \(^{15}\) along different pressure ranges (1.1–137.4 atm). The green and blue lines seen in this figure are linear regressions fitted from experimental data achieved by these authors at 1.1 and 9.6 atm from Helium as bath gas, respectively, providing the expressions

\[
\log k_r (s^{-1}) = 8.224 - 2687.760 \left( \frac{1}{T} \right) \quad \text{(at 1.1 atm)}
\]

and

\[
\log k_r (s^{-1}) = 9.257 - 2902.572 \left( \frac{1}{T} \right) \quad \text{(at 9.6 atm)}
\]

In turn, the equation

\[
\log k_r (s^{-1}) = 13.659 - 4026.637 \left( \frac{1}{T} \right)
\]

(high-pressure limit)

is the result of a linear regression fitted from the ICVT/SCT rate constants obtained here by considering the data presented in Tables 1 and S6 along 200–1000 K (red line in Figure 4). Thus, a comparison between eqs 2 and 4 shows that the HCO → H + CO reaction achieves the high-pressure limit value from ~246 K downward at a pressure of 1.1 atm. Similarly, eqs 3 and 4 indicate 9.6 atm as being the high-pressure limit for the HCO dissociation at temperatures not exceeding ~255 K. However, because the linear behavior is probably not satisfied along the entire temperature range investigated, these values should be considered only as rough high-pressure limit estimates. In this sense, it is worth to mention that further experiments should be accomplished in order to improve the high-pressure limit estimates obtained here for the HCO decomposition at temperatures smaller than ~300 K.

However, as one can also notice in Figure 4, the largest pressure investigated by Hippler et al. \(^{15}\) (137.4 atm) is not large enough to achieve the high-pressure limit for the decomposition reaction into consideration in warmer conditions, along 590–800 K. This finding supports their comments, stating that the rate constants measured experimentally for the HCO dissociation at ~100 atm are “more than one order below the high-pressure limit”. In fact, the rate constant, as exhibited in Table 1, for this reaction at 700 K, 9.57 × 10^{-3} s^{-1}, is 2 orders of magnitude larger than the value of 4.58 × 10^{-5} s^{-1} obtained by these authors at this same temperature and 90.1 atm.

For example, considering now all the rate constants measured by Hippler et al. \(^{15}\) along 1.5–90.1 atm at T = 700 K for the HCO decomposition into H and CO, we obtained a linear regression given by

\[
\log k_r (s^{-1}) = -9.3397 + 0.7213 \log \left( \frac{P \times N_{AV}}{R \times T} \right)
\]

where \(N_{AV}\) is the Avogadro number (in particle mol^{-1}), \(R\) denotes the ideal gas constant (in cm³ atm K⁻¹ mol⁻¹), and \(P\) represents the pressure (in atm). Thus, eq 5 indicates that the pressure must be as large as 9.8 × 10⁴ atm to return the same rate constant value predicted here at the high-pressure limit, 9.57 × 10⁻³ s⁻¹. However, considering these same experimental data achieved by Hippler et al. \(^{15}\) (i.e., between pressures from 1.5 to 90.1 atm obtained at T = 700 K), we verified that 9.8 × 10⁴ atm is provided in this study as a lower estimate to the high-pressure limit for the HCO → H + CO reaction at 700 K. In short, theoretical researchers interested in combustion chemistry simulations should be careful when the aforementioned process is included in a system of reactions because of its complicated pressure-dependence pattern.

Table 2. Gibbs Energy Changes due to Variational Effects (in kcal mol⁻¹), \(\Delta G_{var}\), Displacements of the Maximum Gibbs Energy Position along the Reaction Coordinate (in angstrom), \(\Delta r\), and Deviations (in %), Dev, between ICVT and TST Rate Constants (with Respect to ICVT) Furnished by the CCSD(T)/CBS//CCSD/aug-cc-pVTZ Combination at Different Temperatures (in K), \(T\)

| \(T\) (K) | \(\Delta G_{var}^{a}\) kcal mol⁻¹ | \(\Delta r^{b}\) Å | Dev (%) |
|---|---|---|---|
| 50 | 0.018 | 0.030 | 19.8 |
| 100 | 0.020 | 0.032 | 10.6 |
| 200 | 0.031 | 0.038 | 8.1 |
| 300 | 0.050 | 0.046 | 8.8 |
| 500 | 0.114 | 0.062 | 12.1 |
| 700 | 0.202 | 0.078 | 15.7 |
| 1000 | 0.378 | 0.100 | 20.9 |
| 1500 | 0.761 | 0.130 | 29.1 |
| 2000 | 1.237 | 0.155 | 36.5 |
| 2500 | 1.787 | 0.177 | 43.3 |
| 3000 | 2.402 | 0.196 | 49.6 |
| 3500 | 3.074 | 0.214 | 55.6 |
| 4000 | 3.796 | 0.229 | 61.2 |

“Values defined as the difference between the maximum Gibbs energy encountered along the reaction coordinate (from the ICVT treatment) and the Gibbs energy of the TSRP structure. These displacements are measured from the TSRP structure and following the reaction coordinate to the HCO product side.

reaches 61.2% at 4000 K because of an increase of 3.80 kcal mol⁻¹ in the Gibbs energy of activation along the reaction coordinate (see Table 2).

Taking into account the HCO decomposition into H and CO, Figure 4 shows a comparison between the rate constants obtained in this study (from 200 to 1000 K) for the HCO → H + CO reaction and experimental values measured by Hippler et al. \(^{15}\) along different temperatures (590, 643, 700, 752, and 800 K) and along different pressure ranges (1.1–137.4 atm).
The best results calculated for $k_1$ and $k_2$ between 300 and 2000 K (from the ICVT/SCT treatment, as shown in Table 1) as well as rate constant values from 298 to 373 K, as shown in Table S6 (this table is discussed in more details later), were used to obtain the parameters from modified Arrhenius’ equation given by

$$k_{ ARR} = A \left( \frac{T}{300 \text{ K}} \right)^\beta \exp \left( - \frac{E_{ ARR}}{RT} \right)$$

where $R$ denotes the ideal gas constant, $T$ is the temperature, $A$ stands for the constant term of the pre-exponential factor, $\beta$ accounts for the temperature dependence of the pre-exponential factor, and $E_{ ARR}$ corresponds to Arrhenius’ activation energy.

The parameters, as encountered from eq 6, are listed in Table 3, which reproduce the $k_1$ and $k_2$ values presented in Tables 1 and 6.

| reaction | $A^a$ | $\beta$ | $E_{ ARR}$ (in kcal mol$^{-1}$) | MAD$^b$ |
|----------|-------|---------|-------------------------------|--------|
| H + CO $\rightarrow$ HCO | 2.982 $\times$ 10$^{-11}$ | 1.0271 | 2.64 | 2.1 |
| HCO $\rightarrow$ H + CO | 1.369 $\times$ 10$^{-3}$ | 1.0599 | 17.79 | 5.8 |

“The $A$ values for H + CO $\rightarrow$ HCO and HCO $\rightarrow$ H + CO reactions are given in units of cm$^3$ particle$^{-1}$ s$^{-1}$ and s$^{-1}$, respectively.” MAD means maximum absolute deviations (in %) found between rate constants, as obtained from eq 6, and those presented in Tables 1 and S6.

S6 along 298–2000 K with maximum absolute deviations (MADs) of only 2.1 and 5.8%, respectively. However, although our fittings have provided values for the $\beta$ parameter of only 1.03 and 1.06 (for the H + CO $\rightarrow$ HCO and HCO $\rightarrow$ H + CO reactions, respectively), we notice that the MADs from traditional Arrhenius’ equation along the same temperature range would be much larger, 24.2 and 28.1%, in comparison, respectively, to $k_1$ and $k_2$ data exhibited in Tables 1 and S6. Anyway, traditional Arrhenius’ equations provided activation energy values of 3.89 and 19.07 kcal mol$^{-1}$, which are 1.25 and 1.28 kcal mol$^{-1}$ larger than the $E_{ ARR}$ results, respectively, as exhibited in Table 3, for forward and reverse reactions.

Finally, as discussed in the Introduction section, the experimental activation energy value of 2.0 $\pm$ 0.4 kcal mol$^{-1}$, which was furnished by Wang et al. from fittings of rate constants measured between 298 and 373 K for the H + CO $\rightarrow$ HCO reactions, is under frequent debate by theoreticians. Inspired by these discussions, we decided to calculate ICVT/SCT rate constants for the forward and reverse H + CO $\leftrightarrow$ HCO reactions over the same temperature range investigated by Wang et al. (see Table S6) as well as determining traditional and modified Arrhenius’ parameters from these values (see Table S7). Thus, one can observe, as shown in Table S7, that traditional Arrhenius’ equation fitted for the H + CO $\rightarrow$ HCO reaction furnished now an activation energy value of 3.22 kcal mol$^{-1}$, whereas the modified equation provided 1.96 kcal mol$^{-1}$. The modified equation also indicates a more complicated temperature-dependence pattern because $\beta$ is now close to 1.91. Although the theoretical activation energy value determined at the appropriate temperature range (3.22 kcal mol$^{-1}$) is now closer to the experimental determination, the deviation is still too large. However, we believe that this remaining discrepancy occurs mainly because of the different pressure regimes investigated in each case. Therefore, the data shown in Tables 1, 3, S6, and S7 could be used as a guide for experimentalists interested in studying the H + CO $\leftrightarrow$ HCO reactions at high-pressure limit conditions or in chemical models of combustion processes.

3. CONCLUSIONS

The present study employed a high-level quantum chemistry treatment in order to provide electronic structure properties as well as thermochemical and kinetic data for the forward and reverse H + CO $\leftrightarrow$ HCO reactions. The results obtained here are in good agreement with the previous theoretical and experimental values found in the literature for geometries, vibrational frequencies, and energy differences.

Therefore, this work complements the chemical kinetic knowledge regarding the forward and reverse reactions studied here, which were mostly investigated at low pressures or in fall-off regions, providing accurate rate constants at the high-pressure limit regime along temperatures between 50 and 4000 K. In addition, we carefully analyzed the influence of variational and quantum tunneling effects on rate constants. The relative contributions of the variational effects at the highest temperatures considered are almost as relevant as those from quantum tunneling corrections at the smallest temperatures.

Modified Arrhenius’ equations were fitted over a range from 298 to 2000 K providing recommended activation energies of 2.64 and 17.79 kcal mol$^{-1}$, respectively, for the H + CO $\rightarrow$ HCO and HCO $\rightarrow$ H + CO reactions at the high-pressure regime.

Similarly, traditional Arrhenius equations fitted along this same temperature range furnished activation energies of 3.89 and 19.07 kcal mol$^{-1}$. For comparison, the calculated barrier heights corrected for zero-point energies are 3.68 and 18.08 kcal mol$^{-1}$.

Finally, we determined additional rate constant values along temperatures between 298 and 373 K and used such values to achieve Arrhenius’ parameters. This was done in order to contribute to the common debate seen in the literature regarding the reliability of the reference activation energy of 2.0 $\pm$ 0.4 kcal mol$^{-1}$, which was determined experimentally by Wang et al. for the forward H + CO + M $\rightarrow$ HCO + M reaction by using traditional Arrhenius’ expression fitted at this same temperature interval. Therefore, we obtained an activation energy value equal to 3.22 kcal mol$^{-1}$ in the traditional fitting approach. One can notice that this result is closer to the reference than the barrier height (3.68 kcal mol$^{-1}$) or even the activation energy fitted in a different temperature interval (3.89 kcal mol$^{-1}$), indicating that a significant fraction of the discrepancy between theory and experiment must be ascribed to the improper use of barrier heights instead of Arrhenius’ activation energies or the consideration of inadequate temperature ranges in the fitting procedure to attain activation energies. Anyway, the remaining discrepancies are still too large, and we believe that this deviation is mainly caused by the different pressure regimes considered in each case.

In turn, the kinetic data obtained in the present study could be used as a guide for researchers interested in investigating the H + CO $\leftrightarrow$ HCO reactions at the high-pressure limit. Finally, we roughly estimated high-pressure values of 1.1 (T $\geq$ 246 K), 9.6 (T $\leq$ 255 K), and $\sim$9.8 $\times$ 10$^8$ atm (at 700 K). Therefore, the complicated pressure-dependence pattern exhibited by this reaction suggests that researchers interested in modelling combustion processes including such reaction should be careful about the most appropriate reaction rate values used depending on the experimental conditions investigated.
4. METHODOLOGY

Equilibrium geometries (from very tight convergence criteria) and harmonic vibrational frequencies for stationary point structures [reactants (H and CO), precomplex (PrC), transition state (TSRP), and product (HCO)] along the reaction coordinate were encountered by means of the unrestricted coupled cluster treatment with single and double excitations (CCSD) in combination with the aug-cc-pVTZ basis set. A complete basis set (CBS) extrapolation was posteriorly used to improve electronic energy estimates at these structures (\(E_{CBS}\))

\[
E_{CBS} = E_q - \frac{(E_p - E_q)(q + \frac{1}{2})^4}{(p + \frac{1}{2})^4 - (q + \frac{1}{2})^4}
\]

(with \(p = S\) and \(q = 6\))

where \(E_q\) and \(E_p\) are electronic energies from single-point calculations performed at CCSD/aug-cc-pVTZ optimized geometries, which were achieved from the CCSD treatment including perturbative corrections for triple excitations [CCSD(T)] along with the aug-cc-pV5Z and aug-cc-pV6Z basis sets, respectively. In turn, the analysis of \(T_1\) diagnostic values assures the reliability of the CCSD/aug-cc-pVTZ, CCSD(T)/aug-cc-pV5Z, and CCSD(T)/aug-cc-pV6Z single-reference methodologies. The unrestricted calculations show insignificant signs of spin contamination (the maximum \(S^2\) value was only 0.7823 for doublets). In addition, intrinsic reaction coordinate calculations demonstrated the connection of TSRP with reactants (H + CO) and the product (HCO).

A vibrational scaling factor of 0.956 was adopted in order to obtain estimates of anharmonic vibrational frequencies from our original CCSD/aug-cc-pVTZ harmonic values, consequently including anharmonic corrections to resulting zero-point energies \(\langle \varepsilon_0 \rangle\) and thermal corrections for enthalpies \(\langle \varepsilon_H \rangle\) and Gibbs energies \(\langle \varepsilon_G \rangle\). This procedure is important to provide theoretical estimates of related properties in closer agreement with experimental measurements. Thus, enthalpies \((H)\) and Gibbs energies \((G)\) were determined from the treatment labeled here CCSD(T)/CBS/CCSD/aug-cc-pVTZ, which represents a combined treatment given by

\[
H = E_{CBS} + \varepsilon_0 + \varepsilon_H
\]

and

\[
G = E_{CBS} + \varepsilon_0 + \varepsilon_G
\]

These thermochemical properties were determined along temperatures \((T)\) ranging from 50 to 4000 K, by considering a standard pressure of 1 atm. Consistently, the entropy \((S)\) results presented in this study are trivially achieved from eqs 8 and 9 by means of

\[
S = \frac{H - G}{T}
\]

All the previously mentioned electronic structure treatments were carried out with the Gaussian 09 code by considering the frozen core approach, whereas the Polyrate package and the Gaussrate interface were used posteriorly to determine rate constants for the forward \((k_f)\) and reverse \((k_r)\) \(H + CO \leftrightarrow HCO\) reactions at the high-pressure limit, which was done along the reactional surface built from CCSD/aug-cc-pVTZ calculations. Such rate constants were attained from the conventional TST associated with Wigner’s quantum tunneling factor \((W)\), as well as from the ICVT together with the SCT approximation. Therefore, as mentioned, electronic energies achieved from the CCSD(T)/CBS/CCSD/aug-cc-pVTZ combined treatment and scaled vibrational frequencies were used in order to improve the reactional surface for rate constant determinations.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03267.

Results for equilibrium geometries, fundamental vibrational frequencies, enthalpies, Gibbs energies, entropies, rate constants from 298 to 373 K, and traditional/modified Arrhenius parameters fitted along this same temperature range (PDF).

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**Notes**

The authors declare no competing financial interest.

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