A Proposal for the Mechanism of the CH + CO₂ Reaction

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Supporting Information

ABSTRACT: Few experimental studies on the CH + CO₂ global reaction propose H, CO, and HCO as major products. However, the reaction mechanisms behind this process have not yet been elucidated. Moreover, some intriguing kinetic particularities were noticed in these previous investigations. The advanced theoretical study performed here shows that a CH insertion mechanism is capable of explaining all the experimental data available. Hence, the strong deviations from a traditional Arrhenius behavior ascribed to the rate-determining elementary reaction (the CH insertion step) account for the kinetic particularities observed experimentally. A change in the preferred product channel as temperatures increase (from HCO + CO to H + 2CO) is also predicted to occur due to the HCO decomposition, although the CH depletion rates in typical conditions are not affected by this additional step.

1. INTRODUCTION

Thermal decompositions of small hydrocarbons such as ethane or methane are able to produce the methylidyne radical (CH) with high efficiency.¹ Moreover, the posterior reaction of CH with other molecular compounds (for example, N₂, O₂, and CO₂) are fundamental for understanding the combustion processes.¹⁻³ However, the mechanisms for most reactions involving CH have not been completely elucidated.³

Despite the importance of methylidyne for combustion, to the best of our knowledge, there are only four experimental studies reported about the kinetics of the gas phase reaction between CH and carbon dioxide (CO₂)¹⁻¹.¹

CH + CO₂ → products (1)

Two main product channels are usually mentioned for this reaction: one producing formyl (HCO) and carbon monoxide (CO) and another providing H + 2CO. The first decomposition channel is more exothermic than the second one at 298 K (∼65.0 and ∼49.2 kcal mol⁻¹, respectively).¹ However, since the forward reaction rates for reaction 1 were estimated by means of CH depletion measurements, the relative importance of each channel was not addressed.¹⁻⁴

According to Butler et al.,² the forward rate constant for reaction 1 is (1.9 ± 0.4) × 10⁻¹² cm³ particle⁻¹ s⁻¹ at room temperature. This value is in agreement with the respective measurements from Berman et al.,³ (1.8 ± 0.1) × 10⁻¹² cm³ particle⁻¹ s⁻¹, who also verified the increase of reaction rate constants with temperature (between 297 and 670 K), providing an Arrhenius’ activation energy of 0.69 ± 0.11 kcal mol⁻¹.

More than a decade later, experimental investigations done by Mehlmann et al.⁴ indicated no pressure dependence (between 5 and 80 Torr) for the rate constant of reaction 1 at room temperature, with a value of (2.05 ± 0.15) × 10⁻¹² cm³ particle⁻¹ s⁻¹. However, a more complicated temperature dependence pattern emerged for such rate constants, that is, decreasing slightly from 296 to 400 K and increasing more significantly between 500 and 873 K. Thereby, a preferential product channel change was proposed by them to occur at temperatures around 500 K. Almost simultaneously, Markus et al.¹ performed experiments at higher temperatures (2500–3500 K), finding an Arrhenius’ activation energy of 15.8 kcal mol⁻¹. Hence, due to the huge discrepancy with respect to the aforementioned activation energy result from Berman et al.,³ Markus et al.¹ suggested a non-Arrhenius behavior for the rate constants of reaction 1 along with the explanation already cogitated by Mehlmann et al.¹ Two probable routes have been conjectured for this reaction: abstraction of an oxygen atom from CO₂ by methylidyne and insertion of CH into a CO bond from carbon dioxide.²⁻⁵

Hence, inspired by these discussions, a thermochemical and kinetic study concerning the

\[ \text{CH(X²Π) + CO₂(X^3Σ_g^+) } \leftrightarrow \text{HCO(X²Σ^+) + CO(X^3Σ^+) } \]  

and

Received: August 7, 2019
Accepted: October 3, 2019
Published: October 17, 2019

DOI: 10.1021/acsomega.9b02530
ACS Omega 2019, 4, 17843–17849

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HCO(\(X^2\Sigma^+\)) \(\leftrightarrow\) H\((^2S_{1/2})\) + CO\((\Xi^2\Sigma^+)\) \hspace{1cm} (3)

reactions were performed along temperatures from 50 to 4000 K. To our knowledge, this is the first theoretical chemistry investigation regarding the mechanism of reaction 2. The main goal of this work is to elucidate the kinetic details of the reaction between CH and CO\(_2\) and to verify whether a decisive explanation can be obtained for the particularities noticed experimentally.

2. RESULTS AND DISCUSSION

Two alternative pathways for the CH + CO\(_2\) \(\leftrightarrow\) HCO + CO reaction were found from UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ calculations (see Figure 1, plotted with Molden 5.3). Each path is constituted by three or four elementary steps, involving one precomplex, one postcomplex (PoC1), four intermediate compounds (IM1, IM2, IM3, and IM4), and six transition state (TS) structures (TSR1, TS12, TS23, TS3P, TS14, and TS4P). Anyway, the CH + CO\(_2\) \(\leftrightarrow\) IM1 elementary reaction (CH insertion step) is a common process for both paths. This study also shows that the HCO \(\leftrightarrow\) H + CO reaction proceeds through a single elementary step, so that the TS and postcomplex structures are labeled as TSRP and PoC2, respectively (Figure 1). The ROCCSD method was used to verify whether the small spin contamination signs detected in some structures (IM2, IM3, TS23, TS3P, TS14, and TS4P) can lead to significant differences in geometries or vibrational frequencies.

Supporting Information Tables S1 and S2 furnish equilibrium geometrical parameters encountered at the UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ levels for all stationary points exhibited in Figure 1. The largest deviations with respect to experimental data of Lide\(^6\) for CH, CO\(_2\), HCO, and CO are around 2.5%. In addition, the maximum discrepancies between results from UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ levels were 0.0096 Å for bond distances and 0.8° for bond angles. However, this bond length difference refers to a significantly elongated H–C bond in the TSRP structure (around 1.8 Å), and the two largest remaining discrepancies are only 0.0061 Å (TS4P) and 0.0031 Å (TS23).

In the case of scaled vibrational frequencies of fundamental bands (see Supporting Information Tables S3 and S4), similar results are once more obtained from UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ calculations (maximum discrepancies of 84.7 cm\(^{-1}\)), with the largest deviation of 6.3% with respect to experimental data.

In summary, the small spin contamination signs noticed in some structures do not lead to significant differences in geometries and vibrational frequencies, indicating the reliability of the standard UCCSD/cc-pVDZ treatment.

The best energy values relative to reactants (CH + CO\(_2\)), which were achieved from the ROCCSD(T)/CBS/\(UCCSD/\)cc-pVDZ combined treatment (\(E_{CBS}\) plus scaled zero-point corrections), are illustrated in Supporting Information Figure S1. One can notice that the three-step mechanism to HCO + CO formation is less likely to occur, once the forward IM1 \(\leftrightarrow\) IM4 process exhibits a barrier height of 51.6 kcal mol\(^{-1}\), whereas the largest barrier along the four-step path is only 6.6 kcal mol\(^{-1}\) (IM3 \(\rightarrow\) HCO + CO process). This preferential trend is also observed for relative enthalpies (see Supporting Information Table S5) and relative Gibbs free energies (see Supporting Information Table S6 and Figure 2) along all temperatures considered here (from 50 to 4000 K). Therefore, the four-step path is predicted as the most favorable route for HCO + CO formation.

The CH + CO\(_2\) \(\rightarrow\) HCO + CO reaction is fairly exothermic, exhibiting an enthalpy change of \(-64.4\) kcal mol\(^{-1}\) at 300 K (Table S5). This result is between the reference values of \(-64.0\) kcal mol\(^{-1}\) at 300 K\(^9\) and \(-64.9\) kcal mol\(^{-1}\) at 298 K\(^10\). Gibbs free energy changes for this reaction are predicted as \(-66.2\) and \(-78.8\) kcal mol\(^{-1}\) at 300 and 3500 K (Table S6), respectively. These results are again in excellent agreement with the reference

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Figure 1. Stationary points of the CH + CO\(_2\) \(\leftrightarrow\) HCO + CO and HCO \(\leftrightarrow\) H + CO reactions as obtained at the UCCSD/cc-pVDZ level.
The CH + CO$_2$ reaction is represented by the same velocity law than typical conditions is represented by the same velocity law than.

Figure 2. Gibbs free energy profiles (in kcal mol$^{-1}$) relative to reactants (CH + CO$_2$) for the stationary point structures of the CH + CO$_2$ ↔ HCO + CO and HCO ↔ H + CO reactions, as calculated at the ROCCSD(T)/CBS//UCCSD/cc-pVDZ level.

values of $-65.8$ and $-77.8$ kcal mol$^{-1}$ at 300 and 3500 K, respectively, as well as with $-66.5$ kcal mol$^{-1}$ at 298 K.

The HCO $\rightarrow$ H + CO reaction is endothermic at all temperatures analyzed and presents an enthalpy change of 15.8 kcal mol$^{-1}$ at 300 K (Table S5), which is in great accordance with the reference value of 15.4 kcal mol$^{-1}$ at 298 K. Therefore, the CH + CO$_2$ $\rightarrow$ H + 2 CO reaction is exothermic by $-48.6$ kcal mol$^{-1}$ at this same temperature (Table S5), in excellent agreement with the literature value of $-49.2$ kcal mol$^{-1}$ at 298 K.

As seen by Gibbs free energies presented in Table S6, the HCO $\rightarrow$ H + CO reaction is nonspontaneous at low temperatures and spontaneous at temperatures higher than 700 K. According to this same table, the Gibbs free energy variation at 300 K, 9.5 kcal mol$^{-1}$, is also in great accordance with the reference value of 9.1 kcal mol$^{-1}$ at 298 K.

Rate constants obtained from the ICVT/SCT formalism are shown in Table 1. Numerical simulations (see the next section) demonstrate that the global rate of the CH + CO$_2$ $\rightarrow$ products reaction along several temperatures (from CH depletion rates in typical conditions) is represented by the same velocity law than the first forward elementary step, from these reactants to IM1. Thus, the CH + CO$_2$ $\rightarrow$ IM1 elementary process (CH insertion step) is proved to be the rate-determining step for the CH + CO$_2$ $\rightarrow$ products reaction along all temperatures considered.

Comparisons can be directly done with the experimental data available. Hence, Berman et al. found rate constants for the reaction between CH and CO$_2$ of $(1.8 \pm 0.1) \times 10^{-12}, (2.5 \pm 0.4) \times 10^{-12}$, and $(3.5 \pm 0.3) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, at temperatures of 297, 480, and 670 K. In turn, experimental values of $(1.9 \pm 0.4) \times 10^{-12}$ and $(2.05 \pm 0.15) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ were measured, respectively, by Butler et al. at room temperature and by Mehlmann et al. at 296 K. Finally, the expression fitted by Markus et al. from experimental data resulted in rate constant values of $1.3 \times 10^{-11}, 2.2 \times 10^{-11}$ and $3.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, at 2500, 3000, and 3500 K. The rate constants presented in Table 1 for the CH + CO$_2$ $\rightarrow$ IM1 step $(2.4 \times 10^{-12}, 3.2 \times 10^{-12}, 4.4 \times 10^{-12}, 2.7 \times 10^{-11}, 3.7 \times 10^{-11}$, and $4.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ obtained, respectively, at 300, 500, 700, 2500, 3000, and 3500 K) are in great agreement with the aforementioned data. The largest relative discrepancy occurs at 2500 K, so that the calculated rate constant is twice as large as the experimental result in this case.

Next, Supporting Information Table S7 provides traditional Arrhenius’ parameters ($A = \text{pre-exponential factor}$ and $E_{\text{ARR}} = \text{Arrhenius’ activation energy}$) for all forward elementary steps discussed in this work. In this table, the Arrhenius’ parameters found for the CH + CO$_2$ $\rightarrow$ IM1 step $(2.4 \times 10^{-12}, 3.2 \times 10^{-12}, 4.4 \times 10^{-12}, 2.7 \times 10^{-11}, 3.7 \times 10^{-11}$, and $4.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) are in excellent accordance with the values of $(5.7 \pm 0.9) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $0.69 \pm 0.11$ kcal mol$^{-1}$, which were obtained by Berman et al. from experimental measurements done between 297 and 670 K. This same elementary step furnished $A = 2.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $E_{\text{ARR}} = 10.2$ kcal mol$^{-1}$ along 2500–3500 K, which are respectively in fair agreement with the experimental values of $3.2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $15.8$ kcal mol$^{-1}$ encountered by Markus et al. along this same temperature range.

From the results discussed before, one can conclude that the discrepancies between activation energy values obtained experimentally at low and high temperatures are readily explained by strong temperature dependencies exhibited by the rate-determining elementary process (CH + CO$_2$ $\rightarrow$ IM1).

Table 2 presents the parameters fitted for each elementary step according to the following modified Arrhenius’ equation

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

where $R$ is the ideal gas constant (in kcal mol$^{-1}$ K$^{-1}$), $T$ is the temperature, and $\beta$ is a temperature dependence parameter. This equation provides our recommended rate constant data. As expected, the CH + CO$_2$ $\rightarrow$ IM1 step shows an evident non-Arrhenius behavior once the $\beta$ parameter is 1.87 in this case, which agrees with the proposal from Markus et al. regarding rate constants of reaction 1.

In addition, a kinetic catalogue organized by Baulch et al. is in excellent accordance with the aforementioned data. The largest relative discrepancy occurs at 2500 K, so that the calculated rate constant is twice as large as the experimental result in this case.

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Table 1. Forward, $k_f$, and Reverse, $k_r$, ICVT/SCT Rate Constants (in s$^{-1}$) for Elementary Steps Involved in the CH + CO$_2$ → HCO + CO and HCO ↔ H + CO Reactions Calculated at the ROCCSD(T)/CBS//UCCSD/cc-pVDZ Level and Different Temperatures (in K), $T$.

| $T$ (K) | CH + CO$_2$ → IM1 | IM1 → IM2 | IM2 → IM3 | IM3 → HCO + CO | IM1 → IM4 | IM4 → HCO + CO | HCO ↔ H + CO |
|--------|------------------|-----------|-----------|----------------|-----------|----------------|----------------|
| 50     | 3.42 × 10$^{-12}$ | 4.07 × 10$^8$ | 2.23 × 10$^8$ | 2.09 × 10$^{-13}$ | 5.21 × 10$^{-13}$ | 5.21 × 10$^{-13}$ | 5.21 × 10$^{-13}$ |
| 100    | 2.31 × 10$^{-12}$ | 1.31 × 10$^{10}$ | 9.18 × 10$^{10}$ | 1.27 × 10$^6$ | 4.68 × 10$^{-13}$ | 1.47 × 10$^{-13}$ | 1.26 × 10$^{-13}$ |
| 200    | 2.11 × 10$^{-12}$ | 1.04 × 10$^{11}$ | 6.92 × 10$^{11}$ | 9.68 × 10$^6$ | 5.38 × 10$^{-12}$ | 4.15 × 10$^{-12}$ | 6.62 × 10$^{-12}$ |
| 300    | 2.36 × 10$^{-12}$ | 1.10 × 10$^{12}$ | 1.43 × 10$^{12}$ | 2.74 × 10$^7$ | 1.53 × 10$^{-12}$ | 6.22 × 10$^{-12}$ | 1.49 × 10$^{-12}$ |
| 500    | 3.20 × 10$^{-12}$ | 1.25 × 10$^{13}$ | 2.49 × 10$^{13}$ | 3.30 × 10$^8$ | 7.35 × 10$^{-12}$ | 3.46 × 10$^{-12}$ | 3.32 × 10$^{-12}$ |
| 700    | 4.39 × 10$^{-12}$ | 1.36 × 10$^{14}$ | 3.11 × 10$^{14}$ | 2.72 × 10$^9$ | 1.88 × 10$^{-13}$ | 2.36 × 10$^{-13}$ | 8.20 × 10$^{-13}$ |
| 1000   | 6.73 × 10$^{-12}$ | 1.46 × 10$^{15}$ | 3.69 × 10$^{15}$ | 1.31 × 10$^10$ | 1.72 × 10$^{-13}$ | 5.77 × 10$^{-13}$ | 5.77 × 10$^{-13}$ |
| 1500   | 1.20 × 10$^{-11}$ | 1.51 × 10$^{16}$ | 4.22 × 10$^{16}$ | 4.21 × 10$^{10}$ | 7.95 × 10$^{-13}$ | 1.30 × 10$^{-13}$ | 1.70 × 10$^{-13}$ |
| 2000   | 1.88 × 10$^{-11}$ | 1.50 × 10$^{17}$ | 4.53 × 10$^{17}$ | 7.18 × 10$^{11}$ | 6.22 × 10$^{-13}$ | 1.15 × 10$^{-13}$ | 9.42 × 10$^{-13}$ |
| 2500   | 2.73 × 10$^{-11}$ | 1.50 × 10$^{18}$ | 4.73 × 10$^{18}$ | 7.44 × 10$^{12}$ | 8.48 × 10$^{-13}$ | 1.09 × 10$^{-13}$ | 2.62 × 10$^{-13}$ |
| 3000   | 3.74 × 10$^{-11}$ | 1.50 × 10$^{19}$ | 4.87 × 10$^{19}$ | 7.43 × 10$^{13}$ | 4.81 × 10$^{-13}$ | 1.05 × 10$^{-13}$ | 5.17 × 10$^{-13}$ |
| 3500   | 4.90 × 10$^{-11}$ | 1.50 × 10$^{20}$ | 4.96 × 10$^{20}$ | 7.43 × 10$^{14}$ | 1.66 × 10$^{-13}$ | 1.03 × 10$^{-13}$ | 8.35 × 10$^{-13}$ |
| 4000   | 6.23 × 10$^{-11}$ | 1.50 × 10$^{21}$ | 4.99 × 10$^{21}$ | 7.43 × 10$^{15}$ | 4.16 × 10$^{-13}$ | 1.02 × 10$^{-13}$ | 1.19 × 10$^{-13}$ |

$k_f$ and $k_r$ are in units of cm$^3$ particle$^{-1}$ s$^{-1}$.

Table 2. Modified Arrhenius’ Parameters [$A$ (in s$^{-1}$), $\beta$, and $E_{ARB}$ (in kcal mol$^{-1}$)], Which Were Obtained from ICVT/SCT Rate Constants Calculated for Different Temperature Ranges (in K), $T_R$, for Each Elementary Process Involved in the CH + CO$_2$ → HCO + CO and HCO ↔ H + CO Reactions.

| chemical process | $A$ (s$^{-1}$) | $\beta$ (kcal mol$^{-1}$) | $E_{ARB}$ (kcal mol$^{-1}$) | MAD (%) | $T_R$ (K) |
|------------------|--------------|--------------------------|----------------------------|---------|-----------|
| CH + CO$_2$ ↔ IM1 | 4.208 × 10$^{-13}$ | 1.8735 | −1.04 | 2.7 | 300–4000 |
| IM1 ↔ IM2 | 1.795 × 10$^{13}$ | −0.0548 | 0.30 | 2.8 | 300–4000 |
| IM2 ↔ IM3 | 5.614 × 10$^{12}$ | −0.0042 | 0.82 | 0.8 | 300–4000 |
| IM3 ↔ HCO + CO | 3.058 × 10$^{15}$ | −1.8021 | 10.92 | 10.6 | 700–4000 |
| IM1 ↔ IM4 | 1.941 × 10$^{13}$ | 0.1344 | 51.39 | 4.1 | 500–4000 |
| IM4 ↔ HCO + CO | 1.153 × 10$^{13}$ | −0.1124 | −1.05 | 9.8 | 300–4000 |
| HCO → H + CO | 2.484 × 10$^{13}$ | 0.6391 | 18.20 | 15.1 | 300–4000 |
| IM1 ↔ CH + CO$_2$ | 1.557 × 10$^{14}$ | 0.2852 | 37.99 | 5.4 | 300–4000 |
| IM2 ↔ IM1 | 2.892 × 10$^{12}$ | 0.0457 | 24.86 | 3.0 | 300–4000 |
| IM3 ↔ IM2 | 4.847 × 10$^{12}$ | −0.0355 | 0.07 | 1.0 | 300–4000 |
| HCO + CO ↔ IM3 | 2.163 × 10$^{12}$ | −0.0336 | 12.04 | 15.0 | 700–4000 |
| IM4 ↔ IM4 | 3.928 × 10$^{12}$ | 0.0420 | 11.95 | 3.8 | 500–4000 |
| HCO + CO ↔ IM4 | 2.006 × 10$^{12}$ | 0.8128 | 60.29 | 13.5 | 700–4000 |
| H + CO ↔ HCO | 3.011 × 10$^{11}$ | 0.9343 | 2.43 | 6.0 | 300–4000 |

$A$, $\beta$, and $E_{ARB}$ are in units of cm$^3$ particle$^{-1}$ s$^{-1}$, kcal mol$^{-1}$, and kcal mol$^{-1}$, respectively. MAD means maximum absolute deviations (in %) found between rate constants obtained from eq 4 and those presented in Table 1.

and $E_{ARB}$ = −1.04 kcal mol$^{-1}$ are in excellent accordance with those presented by Bauch et al.\textsuperscript{10}

Finally, temporal evolution simulations were performed for the concentrations of stable species. To this end, we considered initial concentrations of 1.0 × 10$^{13}$ and 1.0 × 10$^{12}$ particle cm$^{-3}$ for CH and CO$_2$, respectively, whereas the initial concentrations for the other molecules were taken as zero. The initial concentrations of reactants were chosen based on the representative values used by experimentalists.\textsuperscript{1–4} All forward and reverse rate constants showed in Table 1 were taken into consideration at temperatures of 200, 300, 500, 700, 2500, and 3500 K.

Figure 3 illustrates the results from these simulations, whereas the Supporting Information Table S8 contains equilibrium concentrations and time to achieve this condition. One can notice that CH and CO$_2$ reach a chemical equilibrium.
considerably faster than HCO, CO, and H at 200 and 300 K, indicating a slow HCO decomposition into CO and H in comparison with the CH insertion step. On the other hand, the simulations performed show that the HCO decomposition is much faster than the CH insertion step at temperatures higher than 700 K.

Chemical equilibrium concentrations for CH, IM1, IM2, IM3, and IM4 are almost negligible, reaching a maximum of $\sim 1 \times 10^{-4}$ particle cm$^{-3}$ at 300 K. Hence, these simulations point out HCO and CO concentrations of $1.0 \times 10^{12}$ particle cm$^{-3}$ at the chemical equilibrium at 200 K, whereas the concentration of H is about $10^5$ times smaller. On the other hand, CO and H concentrations at the chemical equilibrium from 500 to 3500 K are, respectively, $2.0 \times 10^{12}$ and $1.0 \times 10^{15}$ particle cm$^{-3}$, while the HCO concentration decays from $\sim 2 \times 10^{7}$ to $\sim 5 \times 10^1$ particle cm$^{-3}$ at this temperature range.

The previous results show that HCO and CO are the major products from the reaction between CH and CO$_2$ at lower temperatures, while the H + 2 CO products predominate from room temperature upwards. These findings are in some agreement with those of Mehlmann et al. and Markus et al. However, these authors proposed a preferential product channel change as a possible explanation for the complicated behavior of rate constants for reaction 1 along temperature changes. Nevertheless, our investigation shows that the CH depletion rates from the global CH + CO$_2$ → products reaction are dictated by the rate-determining step (CH + CO$_2$ → IM1) along all temperatures considered (for CH concentrations larger than $1 \times 10^5$ particle cm$^{-3}$, approximately).

3. CONCLUSIONS

Two alternative insertion mechanisms (the CH molecule is inserted into one CO bond of carbon dioxide) were found for the CH + CO$_2$ ↔ HCO + CO reaction. These alternative routes share the same initial elementary reaction, and the four-step pathway is much faster than the three-step one. According to this preferential mechanism, the global rate for the CH + CO$_2$ → products process, from CH depletion measurements, follows the rate law ascribed to the first forward elementary reaction (CH + CO$_2$ → IM1), which means the CH insertion step is the rate-determining step.
The rate constants and Arrhenius’ parameters obtained here for the aforementioned elementary process are in excellent agreement with all experimental measurements available in the literature for the global reaction. The strong temperature dependence noticed for the rate-determining step is the cause for the huge discrepancy observed in the activation energy values obtained experimentally at low and high temperatures.

Finally, a change in the preferred product channel for the CH + CO₂ reaction along temperature was also verified, so that the HCO + CO products predominate at lower temperatures, whereas the H + 2 CO channel becomes preferential from 300 K upward. However, this second channel requires only an additional step (HCO → H + CO) occurring soon after the formation of HCO. Anyway, the CH + CO₂ → IMI elementary reaction remains the rate-determining step for the CH depletion rates from the global process CH + CO₂ → products.

4. METHODOLOGY

The Gaussian 09 program was employed for the electronic structure calculations. The unrestricted and restricted open-shell coupled cluster treatments with single and double excitations (CCSD) along with the cc-pVDZ basis set (UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ, respectively) were used to investigate the potential energy surfaces. Accurate equilibrium geometries were obtained from very tight convergence criteria. The potential energy surfaces. Accurate equilibrium geometries (CCSD) along with the cc-pVDZ basis set (UCCSD/cc-pVDZ) were obtained experimentally at low and high temperatures.

The unrestricted and restricted open-shell coupled cluster treatments with single and double excitations (CCSD) along with the cc-pVDZ basis set (UCCSD/cc-pVDZ and ROCCSD/cc-pVDZ, respectively) were used to investigate the potential energy surfaces. Accurate equilibrium geometries were obtained from very tight convergence criteria. The T₁ diagnostic was analyzed to estimate the reliability of the single reference methodology used. Only TS14 (0.045 for UCCSD and 0.065 for ROCCSD) and TS4P (0.056 for UCCSD and 0.034 for ROCCSD) presented T₁ results slightly above the recommended threshold value of 0.045 for doublet, but as these structures refer to the nonpreferential route for the CH + CO₂ → HCO + CO reaction, this fact is not worthy of attention. All transition state (TS) structures found here are genuine, presenting only one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculations assured the direct connection of TSs with their corresponding reactant(s) and product(s). A vibrational scaling factor of 0.947 was adopted to consider anharmonic corrections for vibrational frequencies and, consequently, for zero-point energies (ε₀) and thermal corrections to enthalpies and Gibb’s free energies. However, IRC calculations and the posterior rate constant determinations cannot be carried out with the ROCCSD/cc-pVDZ level due to Gaussian 09 limitations. Therefore, the UCCSD/cc-pVDZ treatment is used after validation with ROCCSD/cc-pVDZ results.

The treatment of electronic energies for stationary points was improved from a Complete Basis Set (CBS) extrapolation \[ E_{CBS} = E_n - \frac{(E_m - E_n)(n + \frac{1}{2})^4}{(m + \frac{1}{2})^4 - (n + \frac{1}{2})^4} (\text{with } m = 4 \text{ and } n = 5) \] where \( E_n \) and \( E_m \) are the electronic energies achieved from single-point calculations including also perturbative corrections for triple excitations done, respectively, with cc-pVQZ and cc-pV5Z basis sets (ROCCSD(T)/cc-pVQZ and ROCCSD(T)/cc-pV5Z), which were done at UCCSD/cc-pVQZ optimized geometries. Hence, considering temperatures from 50 to 4000 K and a standard pressure of 1 atm, enthalpies and Gibb’s free energies are evaluated from a sum of \( E_{CBS} \) with scaled values of \( ε₀ \) and thermal corrections. This same combined treatment (ROCCSD(T)/CBS//UCCSD/cc-pVQZ) was employed to obtain rate constants.

We determined forward \((k_f)\) and reverse \((k_r)\) high pressure limit rate constants from the Improved Canonical Variational Transition State Theory (ICVT) together with the Small-Curvature Tunneling (SCT) approximation. These ICVT/SCT rate constants were estimated by using the Polyrate package and the Gausrate interface, which required around seven thousand calculations to build the minimal energy path and the vibrational adiabatic ground-state potential curve for all elementary processes. This huge number of calculations turns the use of larger basis set than cc-pVQZ unviable to this end considering our actual computational resources. Besides, a factor of 2, due to the rotational symmetry number of CO₂, as well as the value of 27.95 cm⁻¹ from the spin–orbit splitting of the X²Π state of CH, were considered to refine \( k_f \) and \( k_r \) results.

Finally, DLSODE (based on GEAR subroutine) was used to simulate the evolution of molecular concentrations along time.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02530.

Relative electronic energies plus zero-point corrections; equilibrium geometries; fundamental vibrational frequencies; enthalpies; Gibb’s free energies; traditional Arrhenius’ parameters; molecular concentrations at the chemical equilibrium (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank FAPESP for financial support (grant numbers 2010/18743-1, 2014/23714-1, 2017/07707-3, 2018/05691-5, and 2019/07671-4). They also thank CNPq for Postdoctoral and researcher fellowships (grant numbers 168132/2014-1, 305366/2015-7, 307052/2016-8, 404337/2016-3, 407760/2018-0, and 305788/2018-3). They also thank Dr. Luiz F.A. Ferrão for fruitful discussions.

REFERENCES

(1) Markus, M. W.; Roth, P.; Just, T. A shock tube study of the reactions of CH with CO₂ and O₂. Int. J. Chem. Kinet. 1996, 28, 171–179.
(2) Butler, J. E.; Fleming, J. W.; Goss, L. P.; Lin, M. C. Kinetics of CH radical reactions with selected molecules at room temperature. Chem. Phys. 1981, 56, 355–365.
(3) Berman, M. R.; Fleming, J. W.; Harvey, A. B.; Lin, M. C. Temperature dependence of CH radical reactions with O₂, NO, CO and CO₂. Symp. (Int.) Combust. 1982, 19, 73–79.

(4) Mehlmann, C.; Frost, M. J.; Heard, D. E.; Orr, B. J.; Nelson, P. F. Rate constants for removal of CH(D)(¼= 0 and 1) by collisions with N₂, CO, O₂, NO and NO₂ at 298 K and with CO₂ at 298 ≤ T/K ≤ 873. J. Chem. Soc., Faraday Trans. 1996, 92, 2335–2341.

(5) Schaffenaar, G.; Noordik, J. H. Molden: a pre- and post-processing program for molecular and electronic structures. J. Comput.-Aided Mol. Des. 2000, 14, 123–134.

(6) Lide, D. R. CRC Handbook of Chemistry and Physics, 84th ed.; CRC Press LLC: Boca Raton, 2004.

(7) Irikura, K. K. Experimental vibrational zero-point energies: diatomic molecules. J. Phys. Chem. Ref. Data 2007, 36, 389–397.

(8) Bishop, D. M.; Cheung, L. M. Vibrational contributions to molecular dipole polarizabilities. J. Phys. Chem. Ref. Data 1982, 11, 119–133.

(9) Chase, M. W., Jr. Ed. NIST-JANAF Thermochemical Tables, 4th ed.; Götthersburg, MD, 1998.

(10) Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. Evaluated kinetic data for combustion modeling: supplement II. J. Phys. Chem. Ref. Data 2005, 34, 757–1397.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. B.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, 2009.

(12) Lee, T. J.; Taylor, P. R. A diagnostic for determining the quality of single-reference electron correlation methods. Int. J. Quantum Chem. 1999, 36, 199–207.

(13) Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer, H. F., III The C₃H₄ + O₂ reaction mechanism: high-level ab initio characterizations. J. Phys. Chem. A 2000, 104, 9823–9840.

(14) Fukui, K. The path of chemical reactions - the IRC approach. Acc. Chem. Res. 1981, 14, 363–368.

(15) Hratchian, H. P.; Schlegel, H. B. Theory and Applications of Computational Chemistry: the First Forty years; Elsevier: Amsterdam, 2005; p 195.

(16) Johnson, R. D., III NIST Computational chemistry comparison and benchmark database NIST Standard Reference Database, Number 101, Release 2015, 17b. http://cccbdb.nist.gov/.

(17) Peterson, K. A.; Feller, D.; Dixon, D. Chemical accuracy in ab initio thermochemistry and spectroscopy: current strategies and future challenges. Theor. Chem. Acc. 2012, 131, No. 1079.

(18) Truhlar, D. G.; Garrett, B. C. Variational transition state theory. Annu. Rev. Phys. Chem. 1984, 35, 159–189.

(19) Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. Theory of Chemical Reaction Dynamics; CRC Press: Boca Raton, 1985; Vol. 4, p 65.

(20) Zheng, J.; Zhang, S.; Lynch, B. J.; Corchado, J. C.; Chuang, Y.-Y.; Fast, P. L.; Hu, W.-P.; Liu, Y.-P.; Lynch, G. C.; Nguyen, K. A.; Jackels, C. P.; Fernández-Ramos, A.; Ellingson, B. A.; Melissas, V. S.; Vili, J.; Rossi, J.; Coitiño, E. L.; Pu, J.; Alba, T. V.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G. POLYRATE; version 2008; Univ. Minnesota: Minneapolis, 2009.

(21) Zheng, J.; Zhang, S.; Corchado, J. C.; Chuang, Y.-Y.; Coitiño, E. L.; Ellingson, B. A.; Truhlar, D. G. GAUSSRATE; version 2009-A; Univ. Minnesota: Minneapolis, 2009.