

# The rate constant for the CO+H<sub>2</sub>O<sub>2</sub> reaction

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The reaction  $\text{CO} + \text{H}_2\text{O}_2 \rightarrow \text{HOCO} + \text{OH}$  (R1) has been proposed as an important oxidation step for CO in CO/H<sub>2</sub> mixtures at low temperatures. In this paper the rate constant for the reaction at 713 K is determined based on the batch reactor experiments of Baldwin, Walker and Webster [Combust. Flame 15 (1970) 167-172] on decomposition of H<sub>2</sub>O<sub>2</sub> sensitized by CO. A value of  $k_1(713 \text{ K}) = 8.1 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was found. This value is consistent with spin-unrestricted density functional theory. Extrapolation to a wider temperature range through ab initio calculations yields the rate constant  $k_1 = 3.6 \cdot 10^4 \text{ T}^{2.5} \exp(-14425[\text{K}]/\text{T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The results show that the reaction is significantly slower than indicated by an earlier rough estimate and it is probably of minor importance in combustion. The present analysis reconciles the batch reactor data of Baldwin et al. with recent high-level theoretical work on the CO+HO<sub>2</sub> reaction.

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Keywords: CO, H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub>, elementary reaction, kinetic model

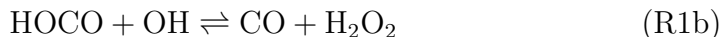
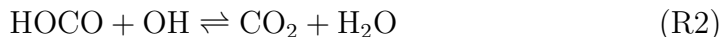
## Introduction

The kinetics of CO/H<sub>2</sub> conversion is generally considered to be well-known. Nevertheless, Petersen et al. [1] have recently demonstrated that there is a substantial discrepancy between the predictions of state-of-art detailed kinetic models [2–6] and experimental data obtained in flow reactors [1, 7], shock tubes [1], and rapid compression machines [8] for ignition of mixtures of H<sub>2</sub> and CO at 20 bar and temperatures of 600–950 K. Under these conditions, the models consistently predict ignition times that are up to five orders of magnitude above experimental values.

At the low temperature/high pressure conditions of these studies, the availability of OH and H radicals is limited by the conversion of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Rasmussen et al. [9] recently proposed the reaction



as a possible major chain branching step in this system. There are no measurements of this reaction reported in literature. The reverse reaction between HOCO and OH has two possible product channels, both exothermic



The HOCO+OH reaction has been studied theoretically by Yu et al. [10]. They found that the reaction is essentially barrierless and exhibits a rate constant ranging from  $6.2 \times 10^{12}$  to  $1.1 \times 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> across 250 to 800 K. However, Yu et al. only considered the pathway to CO<sub>2</sub>+H<sub>2</sub>O (R2), not CO+H<sub>2</sub>O<sub>2</sub> (R1b). According to preliminary scans along the singlet surface for (R1b) at the spin-restricted B3LYP/6-31G(d) level of theory, there is apparently no barrier to the exothermic CO+H<sub>2</sub>O<sub>2</sub> channel [9]. However, this initial computational result should be treated cautiously as multireference methods may be more appropriate at large radical-radical separations. With a rough estimate of  $k_{1b} = 10^{13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, the reaction had a major impact on the predicted ignition delay for CO/H<sub>2</sub> mixtures [9].

A more thorough investigation is desirable for the reaction CO+H<sub>2</sub>O<sub>2</sub>  $\rightleftharpoons$  HOCO+OH (R1). The objective of the present work is to determine  $k_1$  from a reinterpretation of the experimental data of Baldwin et al. [11], combined with ab initio calculations for the reaction. Baldwin et al. conducted batch reactor experiments at 713 K on H<sub>2</sub>O<sub>2</sub> decomposition in the presence of CO.

They used their results to derive a rate constant for the reaction



Their value has been considered to be the most reliable experimental determination of  $k_3$ , but it has been questioned by recent studies, such as the high-level theoretical work of You et al. [12]. In the present work, the experimental results from Baldwin et al. are re-interpreted in terms of a detailed chemical kinetic model with a recent value of  $k_3$ . The objective is to obtain a rate constant for reaction (R1) at 713 K, and explain this value in terms of theory.

## Experimental Interpretation

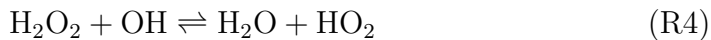
Baldwin et al. [11] investigated the carbon monoxide sensitized decomposition of hydrogen peroxide. The experiments were conducted at atmospheric pressure in a batch reactor at 713 K with an inlet concentration of  $\text{H}_2\text{O}_2$  of about 855 ppm, the CO mole fraction varying from 1.7% to nearly 100%, and  $\text{N}_2$  as balance. The results were reported as  $F(x)$ , where

$$F(x) = \frac{1/(a-x)^{n-1} - 1/a^{n-1}}{n-1}$$

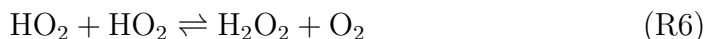
Here,  $a = 100$  and  $x$  is the percentage of homogeneous decomposition of  $\text{H}_2\text{O}_2$ , corrected for a small contribution from surface loss. A value of  $n = 0.7$  was used in the data analysis. Based on the functional expression, Baldwin et al. derived the initial decomposition rate of  $\text{H}_2\text{O}_2$ . The results are shown in Fig. 1.

Our interpretation of the batch reactor data was based on detailed chemical kinetic modeling of the initial decomposition rate data. Except for the value of  $k_1$ , the reaction mechanism and thermodynamic data used in the present work were adopted without modifications from the work of Rasmussen et al. [9], who validated the model for  $\text{CO}/\text{H}_2$  oxidation over a fairly wide range of conditions. The calculations were performed with Senkin [13], which runs in conjunction with the Chemkin library [14]. For each value of the inlet CO concentration,  $k_1$  was fitted to obtain a match between the predicted and measured value of  $d[\text{H}_2\text{O}_2]/dt$ . Only the experiments with CO concentrations  $\geq 50\%$  were included in the fitting procedure.

The results in Fig. 1 clearly show that the initial rate of decomposition of  $\text{H}_2\text{O}_2$  increases with increasing  $[\text{CO}]$ . As explained by Baldwin et al. [11], CO has a sensitizing effect on  $\text{H}_2\text{O}_2$  decomposition due to the competition between the two reactions



The peroxide radical is largely consumed by recombination



and the sequence (R4), (R6) is chain terminating. Since (R5) is chain propagating, the competition between (R4) and (R5) is important for the generation of chain carriers in the system, and this competition explains the sensitizing effect of CO. However, as the CO concentration increases, all the OH radicals eventually react with CO, rather than  $\text{H}_2\text{O}_2$ , and the decomposition rate of  $\text{H}_2\text{O}_2$  should no longer increase with increasing  $[\text{CO}]$ . Such a behavior is not supported by the experimental results. As pointed out by Baldwin et al., the decomposition rate continues to increase even at high CO addition levels (Fig. 1), indicating a second mechanism of acceleration.

Baldwin et al. attributed the acceleration at high CO levels to the chain propagating reaction



which competes with the terminating step (R6). Based on the data, Baldwin et al. derived a value for  $k_3/k_6^{0.5}$ . This expression has been widely accepted as the best way to estimate  $k_3$  [15, 16]. However, recently the reaction has received considerable attention [4, 12, 17–19]. Even though some scatter is observed among experimental and theoretical determinations, there are strong indications that reaction (R6) is considerably slower than indicated by the analysis of Baldwin et al. The most reliable value for the rate constant presumably comes from the theoretical work by You et al. [12]. Calculations of the potential energy surface for  $\text{CO}+\text{HO}_2$  revealed barrier heights of 17.9 and 18.9 kcal/mol for initial trans- and cis-adduct formation respectively. You et al. estimated a value of  $k_3 = 1.6 \times 10^5 \text{T}^{2.18} \exp(-9030/\text{T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the range 300–2500 K, with an estimated uncertainty factor decreasing from a value of 8 at 300 K to below a factor of two at above 1000 K. Most previous determinations of  $k_3$  fall outside the prediction range of You et al., but their value is supported by data from autoignition experiments [17]. Following Rasmussen et al. [9], we have adopted the value of  $k_3$  from You et al. for the present analysis.

In the present work the acceleration of the  $\text{H}_2\text{O}_2$  decomposition by CO at high concentrations is explained by the direct reaction



We have fitted  $k_1$  to match the measured values of  $d[\text{H}_2\text{O}_2]/dt$  at mole fractions of CO of 50% and higher (Fig. 1) with the chemical kinetic model.

The resulting values of  $k_1$  as a function of the CO mole fraction is shown in Fig. 2. The values vary in the range  $(7.6\text{--}8.5) \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , with a weighted mean value of  $k_1 = 8.1 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This value corresponds to a rate constant for the reverse reaction of  $k_{1b} = 7.6 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , i.e. about three orders of magnitude slower than the rough estimate of Rasmussen et al. [9].

The comparison in Fig. 1 shows that the modeling predictions with this value of  $k_1$  (solid line) is in good agreement with the observed initial rate of consumption for  $\text{H}_2\text{O}_2$ , even at CO levels below the range used in the data analysis. The dashed lines, showing modeling predictions for  $k_1 = 0$ , significantly underpredict the  $\text{H}_2\text{O}_2$  consumption rate at CO levels above 20%.

Based on the reported values of  $F(x)$ , we have derived the concentration of  $\text{H}_2\text{O}_2$  as function of time and CO level. In Fig. 3, these results are compared to modeling predictions using the derived value of  $k_1$ . It is seen that the model underpredicts the  $\text{H}_2\text{O}_2$  concentration at longer reaction times, except at low CO levels. The reason for this discrepancy is not known, but it can conceivably be attributed to the effect of side reactions occurring in the gas-phase or on the walls of the reactor.

## Ab Initio Analysis

We have also reanalyzed reaction 1b by ab initio methods implemented in the Gaussian03 program [20]. The reaction between two radical species to form closed shell products may involve degeneracy at long ranges between the singlet and triplet potential energy surfaces, and this is manifested as instability in the closed-shell or spin-restricted Hartee-Fock (RHF) wavefunction. High values of spin contamination are found in the present case, with an expectation value for the square of the spin operator  $\hat{S}^2$  with the spin-unrestricted UHF wavefunction of  $\langle \hat{S}^2 \rangle = 0.91$ . Under some circumstances a useful solution is application of spin-unrestricted density functional

theory (UDFT) [21], and here UB3LYP/aug-cc-pVTZ theory was applied. A transition state (TS) for reaction 1b was located and is shown in Fig. 4. Details of the coordinates and vibrational frequencies are provided in the Appendix. These data were employed in canonical transition state theory (TST) calculations [22]. The electronic partition function of the TS was taken to be 1, together with the electronic partition functions of 2 for trans-HOCO and 3-4 for OH. The structure is essentially planar, except for the terminal H atom which is out of the plane defined by the other atoms. The transition state is therefore chiral, which introduces a symmetry factor of 2 into the TST rate constant [23]. The low frequency mode at  $152\text{ cm}^{-1}$  was identified as rotation of OH about the newly forming O-O bond, and was treated as a hindered rotor by the  $C\omega$  method of Truhlar and coworkers [?]. The barrier height for the transition state, including zero-point vibrational energy, relative to OH + HOCO at infinite separation,  $E_0$ , was chosen as  $26\text{ kJ mol}^{-1}$  to match the point at 713 K derived experimentally via the reverse reaction. The results are shown in Fig. 5 and provide an extrapolation of  $k_{1b}$  to higher temperatures via the expression

$$k_{1b} = 3.9 \times 10^5 T^{2.09} \exp(-2740[\text{K}]/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for 500 - 2000 K. By comparison with the theoretical rate constant  $k_2$  for barrierless H-atom abstraction to make  $\text{H}_2\text{O} + \text{CO}_2$  [10], the branching ratio for CO formation is predicted to be about  $8 \cdot 10^{-4}$  at 700 K. The corresponding  $k_1$  relation is

$$k_1 = 3.6 \times 10^4 T^{2.5} \exp(-14425[\text{K}]/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The barrier was also evaluated theoretically. UB3LYP/aug-cc-pVTZ theory has an expectation value for  $\hat{S}^2$  of  $\langle \hat{S}^2 \rangle = 0.25$  (rather than the value of zero for a closed shell singlet state) and directly yields a value for  $E_0^\ddagger$  of  $43\text{ kJ mol}^{-1}$ . This computed value reflects some mixing with the higher energy triplet state. A proposed sum formula [21,25] yields an energy correction of

$$(E_T - E_{\text{UDFT}}) \times \frac{\langle \hat{S}^2 \rangle_S - \langle \hat{S}^2 \rangle_{\text{UDFT}}}{\langle \hat{S}^2 \rangle_T - \langle \hat{S}^2 \rangle_{\text{UDFT}}}$$

With a triplet  $\langle \hat{S}^2 \rangle_T$  of 2.01 and an energy gap of  $128\text{ kJ mol}^{-1}$  relative to the UDFT singlet, the corrected  $E_0^\ddagger$  is  $25\text{ kJ mol}^{-1}$ . This value is in very good agreement with the experimentally based estimate.

## Conclusions

The rate constant for the reaction  $\text{CO} + \text{H}_2\text{O}_2 \rightarrow \text{HOCO} + \text{OH}$  (R1) at 713 K has been determined based on the batch reactor experiments of Baldwin et al. on decomposition of  $\text{H}_2\text{O}_2$  sensitized by CO. A value of  $k_1(713 \text{ K}) = 8.1 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was found. This value is consistent with spin-unrestricted density functional theory. Extrapolation to a wider temperature range through ab initio calculations yields the rate constant  $k_1 = 3.6 \cdot 10^4 \text{ T}^{2.5} \exp(-14425[\text{K}]/\text{T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The results show that the reaction is significantly slower than indicated by an earlier rough estimate and it is probably of minor importance in combustion. The present analysis reconciles the batch reactor data of Baldwin et al. with recent high-level theoretical work on the  $\text{CO} + \text{HO}_2$  reaction.

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## Appendix

Atomic numbers and Cartesian coordinates for reactants and transition state (in units of 10-10 m)

Hydroxyl

8	0.000000	0.000000	0.108368
1	0.000000	0.000000	-0.866941

HOCO (trans)

8	1.187063	-0.136591	0.000000
6	0.132865	0.386618	0.000000
8	-1.067315	-0.211643	0.000000
1	-1.755166	0.466163	0.000000

Transition state

8	1.924369	-0.459686	-0.031929
6	1.213479	0.432798	0.032439
8	-0.400333	0.332937	0.014202
1	-0.678729	1.256879	0.088840
8	-2.102223	-0.230985	-0.080775
1	-1.976651	-0.991790	0.504545

Vibrational frequencies of reactants and transition at the UB3LYP/aug-cc-pvTZ level of theory, scaled by a factor of 0.97, in  $\text{cm}^{-1}$ : Hydroxyl: 3584

HOCO: 533, 602, 1047, 1202, 1840, 3673

Transition state: 893i, 146, 152\*, 258, 405, 425, 531, 920, 1125, 1981, 3660, 3680

treated as a hindered rotor with a moment of inertia of  $1.54 \cdot 10^{-47} \text{ kg m}^2$ , two distinguishable minima and an internal symmetry number of 1.

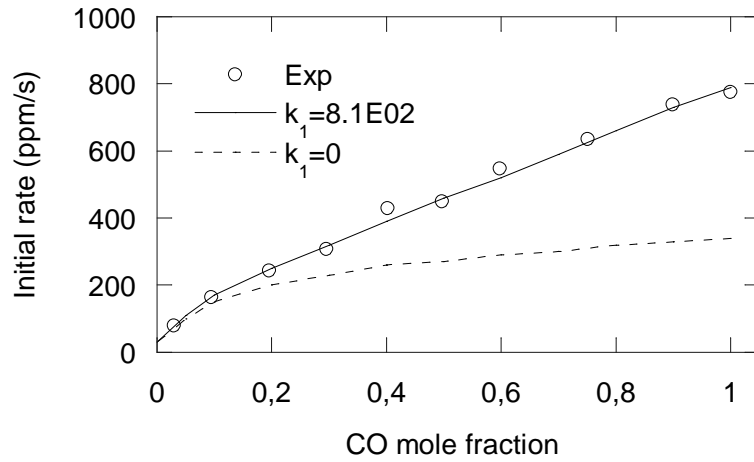


Figure 1: Variation of the initial rate of decomposition of  $\text{H}_2\text{O}_2$  at 713 K as function of the mole fraction of CO. The symbols denote experimental data [11], while the solid and dashed lines denote modeling predictions with  $k_1 = 8.1 \times 10^2$  and  $0 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. Inlet  $\text{H}_2\text{O}_2 = 855 \text{ ppm}$ ; balance  $\text{N}_2$ . Pressure is atmospheric.

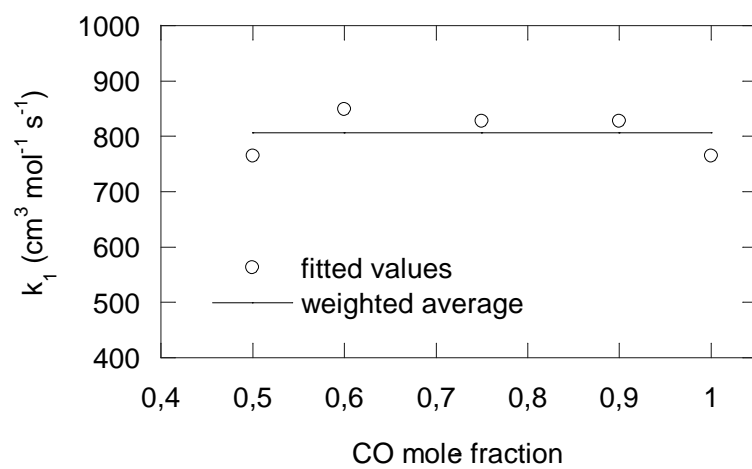


Figure 2: Values of  $k_1$  as function of the mole fraction of CO derived from matching the measured initial rate of decomposition of  $\text{H}_2\text{O}_2$  at 713 K [11] with modeling predictions.

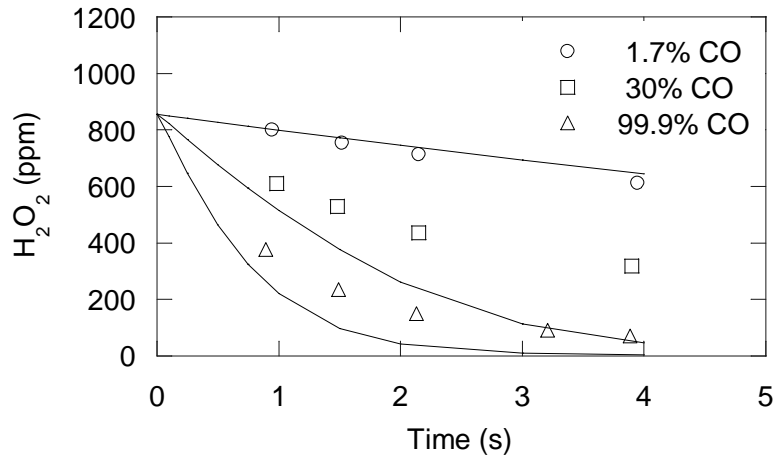


Figure 3: Comparison between the measured [11] and predicted mole fractions of H<sub>2</sub>O<sub>2</sub> as function of time and CO inlet level. The measured values, shown as symbols, were derived from the reported values of F(x). Inlet H<sub>2</sub>O<sub>2</sub> = 855 ppm; balance N<sub>2</sub>. Pressure is atmospheric.

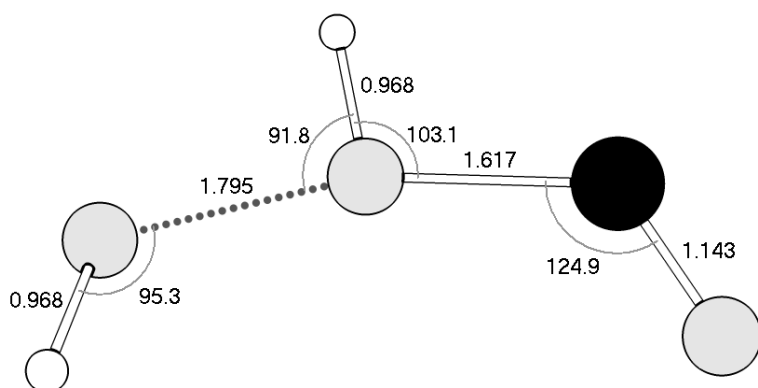


Figure 4: UB3LYP/aug-cc-pVTZ transitions state geometry for the reaction  $\text{HOCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}_2$ . Distances in units of  $10^{-10}$  m and angles in degrees.

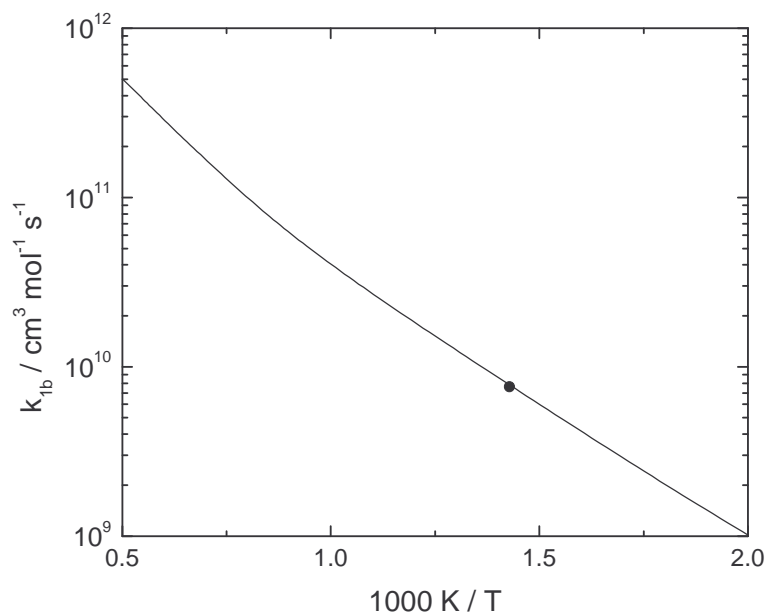


Figure 5: Arrhenius plot of rate constant  $k_{1b}$  for  $\text{HOCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}_2$  derived from the present reinterpretation of the data from Baldwin et al. [11] (●) and the transition state theory fit (solid line).