Chemical Physics Letters 475 (2009) 40–43

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

The rate constant for the $CO + H_2O_2$ reaction

Peter Glarborg [a,*], Paul Marshall [b]

[a] Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
[b] Department of Chemistry and Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, 1155 Union Circle #305070, TX 76203-5017, United States

A R T I C L E I N F O

Article history:
Received 3 April 2009
In final form 13 May 2009
Available online 18 May 2009

A B S T R A C T

The rate constant for the reaction $CO + H_2O_2 \rightarrow HOCO + OH$ (R1) at 713 K is determined based on the batch reactor experiments of Baldwin et al. [R.R. Baldwin, R.W. Walker, S.J. Webster, Combust. Flame 15 (1970) 167] on decomposition of H_2O_2 sensitized by CO. The value, $k_1(713\,K) = 8.1 \times 10^2\ cm^3\ mol^{-1}\ s^{-1}$, is consistent with spin-unrestricted density functional theory. Extrapolation to a wider temperature range through ab initio calculations yields the rate constant $k_1 = 3.6 \times 10^4 T^{2.5} \exp(-14425[K]/T)\ cm^3\ mol^{-1}\ s^{-1}$. The reaction 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 $CO + HO_2$ reaction.

1. Introduction

The kinetics of CO/H_2 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_2 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. Recent work by Chaos and Dryer [9,10] indicates that the observed discrepancies may be attributed mostly to impurities, but it is of interest also to investigate potential uncertainties in the CO/H_2 reaction system.

At the low temperature/high pressure conditions of these studies, the availability of OH and H radicals is limited by the conversion of HO_2 and H_2O_2. Rasmussen et al. [11] recently proposed the reaction

$$CO + H_2O_2 \rightleftharpoons HOCO + OH \tag{R1}$$

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

$$HOCO + OH \rightleftharpoons CO_2 + H_2O \tag{R2}$$

$$HOCO + OH \rightleftharpoons CO + H_2O_2 \tag{R1b}$$

The HOCO + OH reaction has been studied theoretically by Yu et al. [12]. They found that the reaction is essentially barrierless and exhibits a rate constant ranging from 6.2×10^{12} to $1.1 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ across 250–800 K. However, Yu et al. only considered the pathway to $CO_2 + H_2O$ (R2), not $CO + H_2O_2$ (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 $CO + H_2O_2$ channel [11]. However, this initial computational result was treated cautiously as multireference methods may be more appropriate at large radical–radical separations. With a rough estimate of $k_{1b} = 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$, the reaction had a major impact on the predicted ignition delay for CO/H_2 mixtures [11].

A more thorough investigation is desirable for the reaction $CO + H_2O_2 \rightleftharpoons HOCO + OH$ (R1). The objective of the present work is to determine k_1 from a reinterpretation of the experimental data of Baldwin et al. [13], combined with ab initio calculations for the reaction. Baldwin et al. conducted batch reactor experiments at 713 K on H_2O_2 decomposition in the presence of CO. They used their results to derive a rate constant for the reaction

$$CO + HO_2 \rightleftharpoons CO_2 + OH \tag{R3}$$

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. [14]. In the present work, the experimental results from Baldwin et al. are reinterpreted 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 confirm this value in terms of theory.

2. Experimental interpretation

Baldwin et al. [13] investigated the carbon monoxide sensitized decomposition of hydrogen peroxide. The experiments were

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* Corresponding author.
E-mail address: pgl@kt.dtu.dk (P. Glarborg).

0009-2614/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cplett.2009.05.028

conducted at atmospheric pressure in a batch reactor at 713 K with an inlet concentration of H_2O_2 of about 855 ppm, the CO mole fraction varying from 1.7% to nearly 100%, and N_2 as balance. In order to extrapolate their data to obtain initial rates, Baldwin et al. used a method they had introduced in a companion paper [15]. Under many conditions the percentage decomposition of the hydrogen peroxide is quite high, even with the shortest contact times of their study, and direct determination of initial reaction rates would be unreliable. For this reason, Baldwin et al. introduced a functional expression $F(x)$, which exhibited a linear portion at early reaction times, facilitating extrapolation. The function was given as [13,15]

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

Here, $a = 100$ and x is the percentage of homogeneous decomposition of H_2O_2, corrected for a small contribution from surface loss. A value of $n = 0.7$ was used in the data analysis. Based on this functional expression, Baldwin et al. were able to derive the initial decomposition rate of H_2O_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. [11], who validated the model for CO/H_2 oxidation over a fairly wide range of conditions. The calculations were performed with Senkin [16], which runs in conjunction with the Chemkin library [17]. For each value of the inlet CO concentration, k_1 was fitted to obtain a match between the predicted and measured value of $d[H_2O_2]/dt$. Only the experiments with CO concentrations $\geqslant$50% were included in the fitting procedure.

The results in Fig. 1 clearly show that the initial rate of decomposition of H_2O_2 increases with increasing [CO]. As explained by Baldwin et al. [13], CO has a sensitizing effect on H_2O_2 decomposition due to the competition between the two reactions

$$H_2O_2 + OH \rightleftharpoons H_2O + HO_2 \tag{R4}$$

$$CO + OH \rightleftharpoons CO_2 + H \tag{R5}$$

The hydroperoxy radical is largely consumed by recombination

$$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2 \tag{R6}$$

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 H_2O_2, and the decomposition rate of H_2O_2 should no longer increase with increasing [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.

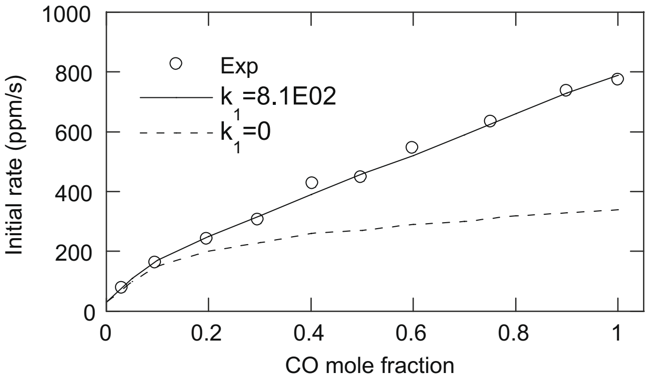

Fig. 1. Variation of the initial rate of decomposition of H_2O_2 at 713 K as function of the mole fraction of CO. The symbols denote experimental data [13], while the solid and dashed lines denote modeling predictions with $k_1 = 8.1 \times 10^2$ and 0 $cm^3\ mol^{-1}\ s^{-1}$, respectively. Inlet $H_2O_2 = 855$ ppm; balance N_2. Pressure is atmospheric.

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

$$CO + HO_2 \rightleftharpoons CO_2 + OH \tag{R3}$$

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 [18,19]. However, recently the reaction has received considerable attention [4,14,20–22]. 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. [14]. Calculations of the potential energy surface for $CO + HO_2$ 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 $k_3 = 1.6 \times 10^5 T^{2.18} \exp(-9030/T)\ cm^3\ mol^{-1}\ s^{-1}$ 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 [20]. Following Rasmussen et al. [11], we have adopted the value of k_3 from You et al. for the present analysis.

In the present work the acceleration of the H_2O_2 decomposition by CO at high concentrations is explained by the direct reaction

$$CO + H_2O_2 \rightleftharpoons HOCO + OH \tag{R1}$$

We have fitted k_1 to match the measured values of $d[H_2O_2]/dt$ 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 are shown in Fig. 2. The values vary in the range $(7.6–8.5) \times 10^2\ cm^3\ mol^{-1}\ s^{-1}$, with a weighted mean value of $k_1 = 8.1 \times 10^2\ cm^3\ mol^{-1}\ s^{-1}$. This value corresponds to a rate constant for the reverse reaction of $k_{1b} = 7.6 \times 10^9\ cm^3\ mol^{-1}\ s^{-1}$, i.e. about three orders of magnitude slower than the rough estimate of Rasmussen et al. [11].

The comparison in Fig. 1 shows that the modeling predictions with this value of k_1 (solid line) are in good agreement with the observed initial rate of consumption for H_2O_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 H_2O_2 consumption rate at CO levels above 20%.

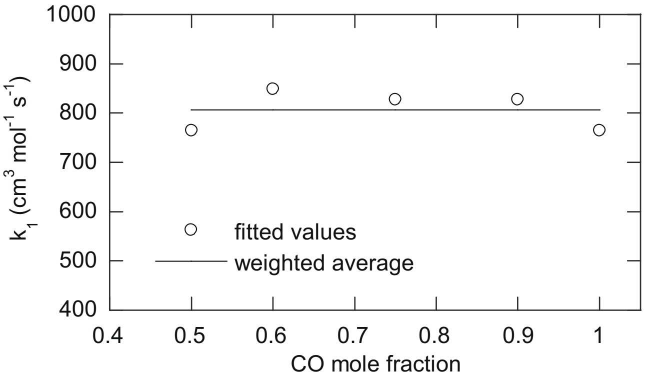

Fig. 2. Values of k_1 as function of the mole fraction of CO derived from matching the measured initial rate of decomposition of H_2O_2 at 713 K [13] with modeling predictions.