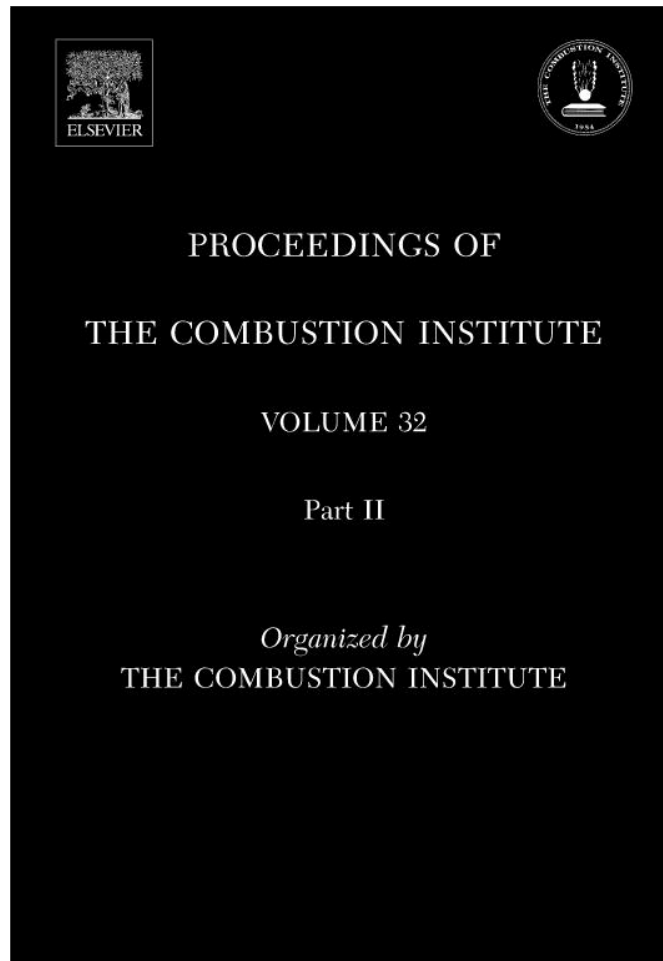


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



ELSEVIER

Available online at www.sciencedirect.com ScienceDirect

Proceedings of the Combustion Institute 32 (2009) 2535–2542

**Proceedings
of the
Combustion
Institute**

www.elsevier.com/locate/proci

Promotion or inhibition of hydrogen–air ignition by iron-containing compounds

Gregory T. Linteris^{a,*}, Valeri I. Babushok^b^a *Fire Research Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8665,
Gaithersburg, MD 20899, USA*^b *Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg,
MD 20899, USA*

Abstract

The ignition of stoichiometric and fuel-lean hydrogen–air mixtures near 1000 K was studied, for varying amounts of iron additives. Depending on the initial conditions, the addition of iron pentacarbonyl promotes or inhibits the ignition of hydrogen/air mixtures. The simulations show that iron compounds at 1 $\mu\text{L/L}$ ¹ reduce the ignition delay by about 30%, and that 50 $\mu\text{L/L}$ can reduce the ignition delay by a factor or two or three for lean and stoichiometric conditions; at slightly higher volume fraction ($>150 \mu\text{L/L}$), the ignition is retarded. The effectiveness of the iron compounds is influenced by the form of the added iron, stoichiometry, and initial temperature of the mixture. At low additive volume fraction, the promotion is the result of relatively fast decomposition of iron pentacarbonyl, which provides a source of radicals at the initial reaction stage during radical pool build-up; the ignition promotion is proportional to the amount of iron-containing additive, and mostly does not involve cycling reactions. In contrast, at higher additive volume fraction, the ignition is retarded by the iron compounds, through catalytic radical recombination cycles similar to those acting in flame inhibition. The reduction in chain-carrying radical concentrations occurs at later times in the ignition process when the radicals have reached high concentrations.

Published by Elsevier Inc. on behalf of The Combustion Institute.

Keywords: Hydrogen fire safety; Hydrogen ignition; Ignition promotion; Ignition sensitization; Iron pentacarbonyl

1. Introduction

Understanding the ignition and detonation behavior of hydrogen in air is important for its safe use as an energy carrier. While the flammability limits and ignition behavior for pure H_2 -air mixtures have been well-documented, comparatively less has been done for these reactants in

the presence of trace contaminants. Since use of hydrogen as a fuel for commercial or residential fuel cells will result in a wider range of ambient conditions, understanding the potential for ignition promotion in the presence of contaminants is warranted. The present study investigates how iron, in various forms, affects the ignition propensity of hydrogen–air mixtures. Iron was chosen because it is known to be the strongest chemical inhibitor for hydrocarbon–air mixtures [1] and it was found to promote combustion under some conditions [2]. Research showed that metal compounds might promote radical formation in

* Corresponding author. Fax: +1 301 975 4052.

E-mail address: linteris@nist.gov (G.T. Linteris).

¹ Note that $\mu\text{L/L}$ is equivalent to ppm by volume.

certain flame situations [3], and shock-tube experiments [4,5] demonstrated that iron-containing additives (and other metals) can promote hydrocarbon ignition. Although it is ultimately planned to assess the effects of other, more common trace contaminants on H₂-air ignition, the present study was undertaken to explore the relevant chemical principles in hydrogen-air ignition promotion using additives for which the effect might be very strong, yet which, because of their low concentrations, maintain nearly constant fuel-air equivalence ratio (ϕ) and final temperature. The parameter used to describe the ignition propensity of the H₂-air mixtures is the ignition delay for a homogeneous, adiabatic, gas-phase mixture. The present work determines the ignition delay through numerical calculations using validated, detailed chemical kinetic models.

2. Background

The effect of metals on ignition has been studied experimentally in both shock-tube and flame configurations. Dolan and Dempster [6] studied the effect of small particles of metal compounds on suppressing the spark ignition of premixed natural gas-air mixtures. They found that sodium bicarbonate was the most effective, while compounds of barium, copper, and cobalt were less effective. Morrison and Scheller [7] investigated the effect of twenty flame inhibitors on increasing the hot-wire ignition temperature of hydrocarbon mixtures, and found that SnCl₄ was the most effective inhibitor tested; whereas the powerful flame inhibitors CrO₂Cl₂ and Fe(CO)₅ had no effect. In flash photolysis studies, Erhard and Norrish [8], found that Pb(C₂H₅)₄ and Te(CH₃)₂ retarded hydrocarbon oxidation, whereas Ni(CO)₄, Fe(CO)₅, and Cr(CO)₆ had a promotion effect.

Several studies demonstrated that metals can promote or retard ignition. In shock-tube studies, Matsuda and co-workers [9] found that Cr(CO)₆, at volume fractions up to 50 μ L/L, reduced the initiation time for reaction of CO or C₂H₂ with O₂. The mode of action was believed to be gas-phase reactions involving CrO, CrO₂, and CrO₃. Matsuda [10] found that a volume fraction of Fe(CO)₅ of a few hundred μ L/L (in CO-O₂-Ar) greatly accelerated the consumption of CO. They postulated the effect to be due to oxidation of CO by metal oxides via: FeO + CO \Rightarrow Fe + CO₂ in their bone-dry mixtures ($X_{OH} \approx 5 \mu$ L/L). In CH₄-O₂-Ar mixtures, Park et al. [4] found that with 500, 1000, or 2000 μ L/L of Fe(CO)₅, the shock-tube ignition time was shorter than without the additive, again indicating a promotion effect of the metal additive; however, they did not determine the cause of the promotion for this moist system. On the other hand, with similar condi-

tions, but *ethane* as the fuel, Shin et al. [5] found that 1000 μ L/L or 2000 μ L/L of Fe(CO)₅ had a distinct inhibition effect on the ignition delay time.

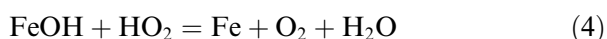
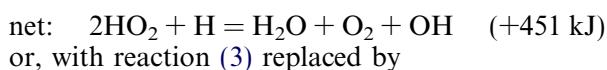
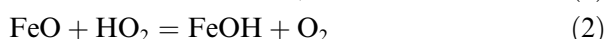
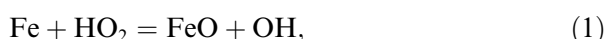
It is well known that the H₂-O₂ mixture can be sensitized by NO, NO₂, and NH₃ [11–15], as well as by HBr [16–18] and HCl [16]. Lovachev and co-workers [17,18] have performed detailed numerical predictions of the shifting promotion or inhibition of H₂-O₂ ignition by HBr, as a function of reaction time, temperature, pressure, and stoichiometry. Moen et al. [19] performed experiments and modeling on the influence of CF₃Br, CF₄, and CO₂ on the detonability of ethane-air and ethane- and hydrogen-oxygen mixtures, and found that the inhibition ability of CF₃Br was greatly reduced as compared to flame inhibition, and that CF₃Br was a sensitizer for some situations. Similarly, Babushok et al. [20] computationally studied the ignition delay of hydrocarbon (H₂, CH₄, CH₃OH, and C₂H₆)-air mixtures with various halogenated fire suppressants (Br₂, HBr, CH₃Br, CF₃Br, and CF₃H). They found that for CF₃Br addition to either H₂- or CH₄-air systems (stoichiometric, 900 K, 1.0 bar), a minimum in the ignition delay (about a 40% reduction) occurred at around 1% CF₃Br. Above this volume fraction, the ignition delay increased rapidly, such that ignition suppression rather than promotion was observed. Studies in detonation tubes have also shown that combustion of hydrocarbons can be alternatively suppressed or enhanced by various halogenated compounds, depending upon the conditions [21]. For the H₂-O₂ system with added metals, however, data and analysis have not yet been presented.

3. Kinetic model

The time-dependent chemical kinetic behavior of the closed, homogeneous system of reactants was modeled with the Sandia SENKIN program [22], with the CHEMKIN [23] subroutines. The program solves the conservation equations for mass and energy, in the present case for an adiabatic constant pressure system ($P = 1.01$ bar). The NIST program Xsenkplot [24] was used for post-processing and reaction pathway analysis allowed determination of key reactions. The chemical kinetic model used was that of Linteris et al. [25]. In that mechanism, the CO/H₂/O₂ system is from Allen and Yetter [26], based upon that from Kim et al. [27], while the iron inhibition mechanism is from Rumminger et al. [28]. As for experimental validation of the mechanism, the CO/H₂/O₂ sub-mechanism has been extensively validated against existing flow reactor, shock-tube, and static reactor experimental data as discussed in Ref. [27], while the iron sub-mechanism has been validated using flame speed data [25,28,29] and diffusion flame extinction data [30]. The CO/H₂/O₂ sub-mechanism has 20 spe-

cies and 92 reactions, and the iron mechanism, 12 species and 55 reactions as described in Refs. [26,28], respectively.

The iron pentacarbonyl inhibition mechanism [28] was developed to describe conditions relevant to hydrocarbon–air flame inhibition. Because of the important role of the HO₂ radical in H₂–O₂ ignition, however, several additional reactions of HO₂ with iron-containing species were considered. In particular, the chain de-branching reactions suggested by Benson [31] (in discussing the effects of lead on engine knock), which follow the HO₂ surface destruction arguments of Pitz and Westbrook [32], may have analogous reactions for iron:



Reaction (3) is already included in the mechanism of Rumminger et al. [28], and rates of reactions (1)–(4) are estimated to be: $2.5 \times 10^{13} e^{-16.6/T}$, $3 \times 10^{12} e^{-8.3/T}$, and $2.0 \times 10^{10} e^{-45.7/T}$, respectively (units: K, J, mol, cm³, s).

In the present work, the ignition delay τ was assumed as the time required for the mixture to rise 400 K above the initial temperature (typically around 1000 K). While this definition is somewhat arbitrary, it provides estimation of a characteristic time of sharp temperature increase related to the ignition process.

4. Results and discussion

The calculated ignition delay τ of a hydrogen–air mixture at 1000 K and 1 bar and $\phi = 1.0$ (left frame) and $\phi = 0.15$ (right frame) is shown in Fig. 1 for iron-containing species added as Fe(CO)₅, or as the intermediate species Fe, FeO, or FeOH. Also shown (and discussed below) is the reduction in τ with added H atom (plotted as the H-atom volume fraction divided by 14 or 1.5, for $\phi = 1.0$ or 0.15, respectively), as well as with added Ar.

The effectiveness of iron in promoting the ignition of hydrogen depends upon both the amount of the iron compound added and the parent iron moiety. As indicated in Fig. 1, the ignition delay drops rapidly for low additive volume fractions (X_a) of iron compounds, but then rises as X_a increases. For $\phi = 1.0$ (left frame in Fig. 1), 1 $\mu\text{L/L}$ of FeO reduces τ by about 35% compared to the pure reactants, and the maximum reduction of about a factor of three is achieved at 150 $\mu\text{L/L}$ of FeO. Beyond that concentration, τ begins to rise. Near the lean flammability limit ($\phi = 0.15$, right frame), the neat reactants have a 50% longer ignition delay than in the stoichiometric case. FeO at 1 $\mu\text{L/L}$ gives a similar reduction (30%) in τ , and the maximum reduction is about a factor of two at 50 $\mu\text{L/L}$.

Different iron-containing species have different level of influence. Thus Fe(CO)₅ and Fe are about equally as effective, whereas FeOH, and especially FeO, are significantly more effective. The calculated species profiles and reaction fluxes indicate that Fe(CO)₅ decomposes to Fe relatively quickly, and hence, Fe(CO)₅ and Fe show comparable promotion. Calculations with Fe + 5 CO show that the differences in τ between Fe and Fe(CO)₅ are not due to the presence of the CO fragments,

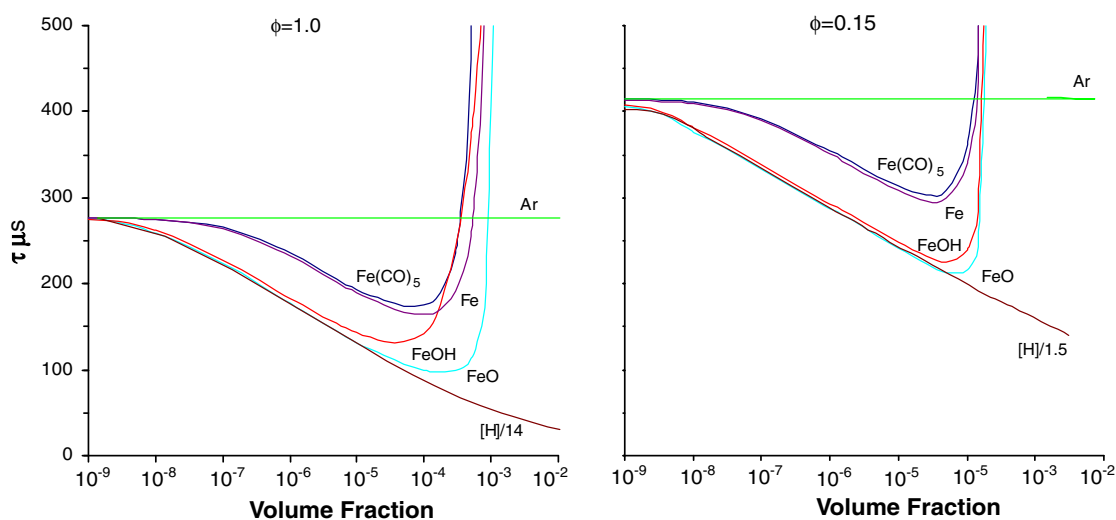


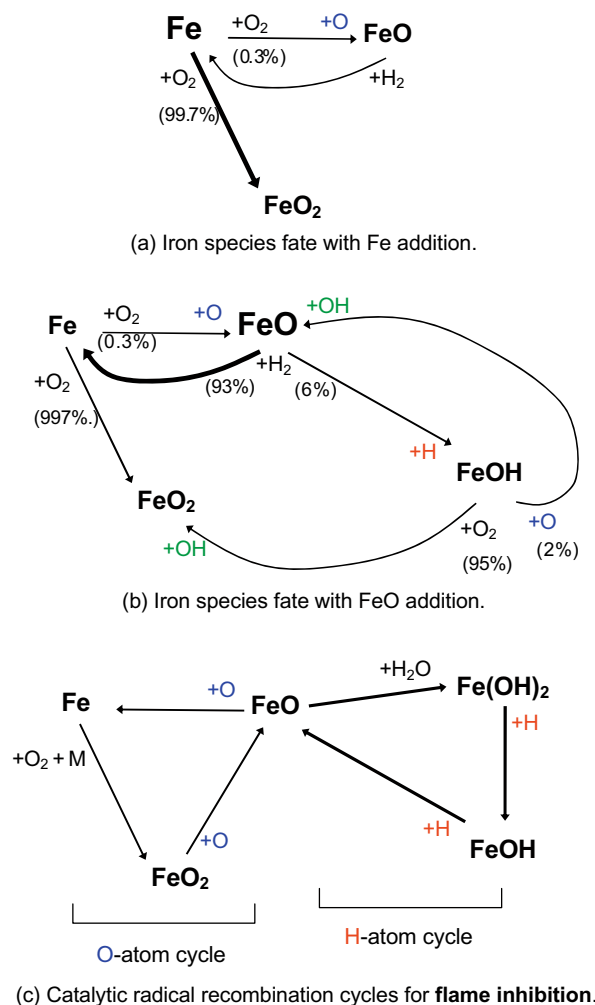
Fig. 1. Calculated ignition delay τ for H₂–air mixture ($T = 1000 \text{ K}$, $P = 1 \text{ bar}$) with Ar, Fe(CO)₅, Fe, FeOH, FeO, or H atoms added at varying volume fraction (log scale), (left frame: $\phi = 1.0$, right frame, $\phi = 0.15$).

but rather, to the rate limitations in the decomposition of $\text{Fe}(\text{CO})_5$.

Additional calculations, in which the activation energy for the initial decomposition step for $\text{Fe}(\text{CO})_5$ is varied, indicate that the ignition delay (for $\phi = 1.0$, $X_{\text{Fe}(\text{CO})_5} = 25 \mu\text{L/L}$, and $900 \text{ K} \leq T \leq 1050 \text{ K}$) was unaffected for $E_a \leq 188 \text{ kJ/mol}$, but changed significantly for values above that (note, $E_a = 167 \text{ kJ/mol}$ in the present model). Thus, depending upon the decomposition rate of the initial metal compound, and the characteristic time of radical build-up, there can be either an increase or a decrease in τ , depending upon the initial temperature. To avoid potential complications (due to the finite rate of $\text{Fe}(\text{CO})_5$ decomposition) in interpretation of the effect of iron on ignition, the discussion below focuses on the effects of intermediate species Fe, FeO, and FeOH, which provide an upper limit to the effect of the iron species on ignition, helping to clarify the salient kinetic effects of the metal additives.

To understand the reasons for the varying behavior of the different forms of iron, the reaction fluxes at early times ($0 \leq t \leq 2.5 \mu\text{s}$) were examined at $X_a = 50 \mu\text{L/L}$ (for Fe or FeO addition), which is near to X_a of minimum τ . Figure 2a and b illustrate the major reactions of iron species in $\text{H}_2\text{-O}_2$ ignition with added Fe or FeO, while Fig. 2c shows the comparable figure for iron-species inhibition of hydrocarbon–air flames. For the case of Fe addition (Fig. 2a), nearly all (99.7%) of the Fe reacts with O_2 to form FeO_2 . Since the main reaction for FeO_2 consumption is its reaction with O atom, FeO_2 is not significantly consumed, and builds in concentration, until the main radical pool build-up occurs. That is, the species FeO_2 represents a sink for iron species during build-up of the radical pool. On the other hand, a small fraction (0.3%) of the Fe reacts with O_2 to form $\text{FeO} + \text{O}$, and ignition promotion occurs from the O atom directly formed, which is consumed primarily via the chain-branching reaction: $\text{O} + \text{H}_2 \Rightarrow \text{OH} + \text{H}$. The FeO which is formed reacts mostly with H_2 via $\text{FeO} + \text{H}_2 \Rightarrow \text{Fe} + \text{H}_2\text{O}$, to reform Fe (and form H_2O which also builds up). Hence, Fe addition serves to inject radicals into the system at early times, and the magnitude of the radical addition is determined by the amount of Fe added and the ratio of the rates of $\text{Fe} + \text{O}_2 + \text{M} \Rightarrow \text{FeO}_2 + \text{M}$ and $\text{Fe} + \text{O}_2 \Rightarrow \text{FeO} + \text{O}$.

For the case of FeO addition (Fig. 2b), most (93%) of the FeO reacts with H_2 via $\text{FeO} + \text{H}_2 \Rightarrow \text{Fe} + \text{H}_2\text{O}$, and the Fe reacts with O_2 to form FeO_2 , which along with the H_2O , reacts slowly and builds up in the system (as described above). On the other hand, about 6% of the FeO reacts via $\text{FeO} + \text{H}_2 \Rightarrow \text{FeOH} + \text{H}$ to form H atoms directly, and FeOH reacts mostly with O_2 to form FeO_2 and OH. Hence, FeO addition



(c) Catalytic radical recombination cycles for flame inhibition.

Fig. 2. Iron species - radical reactions in $\text{H}_2\text{-O}_2$ ignition ($0 \leq t \leq 2.5 \mu\text{s}$, $50 \mu\text{L/L}$ of additive, $T = 1000 \text{ K}$, $P = 1.01 \text{ bar}$, $\phi = 1.0$). The species name (e.g., $+\text{H}$) at the start of the arrow indicates the reaction partner, and the numbers in parentheses indicate the fraction of the reaction flux of that species proceeding through the given path.

leads to a much higher early injection of radicals into the system than does Fe addition. This is illustrated in Fig. 1 which plots τ with H atoms added directly with the reactants; the effect of the H atoms is plotted as a function of $[\text{H}]$ scaled by some factor (14 for $\phi = 1.0$, and 1.5 for $\phi = 0.15$), highlighting the result that only some portion of the added FeO is converted to H-atoms early in the time history. The early injection of radicals at short times with FeO addition is also illustrated in Fig. 3, which shows the temperature and H-atom volume fraction as a function of time with (0, 2, 20, 200 and 2000) $\mu\text{L/L}$ of FeO added to stoichiometric $\text{H}_2\text{-air}$. Clearly, with increasing FeO addition, there is an increasing offset in the profiles of $[\text{H}]$, which all increase with time. Note that at the inlet condition, ($P = 1 \text{ bar}$ and $T = 1000 \text{ K}$) equilibrium X_{H} , is about 10^{-12} ; whereas, under adiabatic conditions with constant enthalpy and pressure,

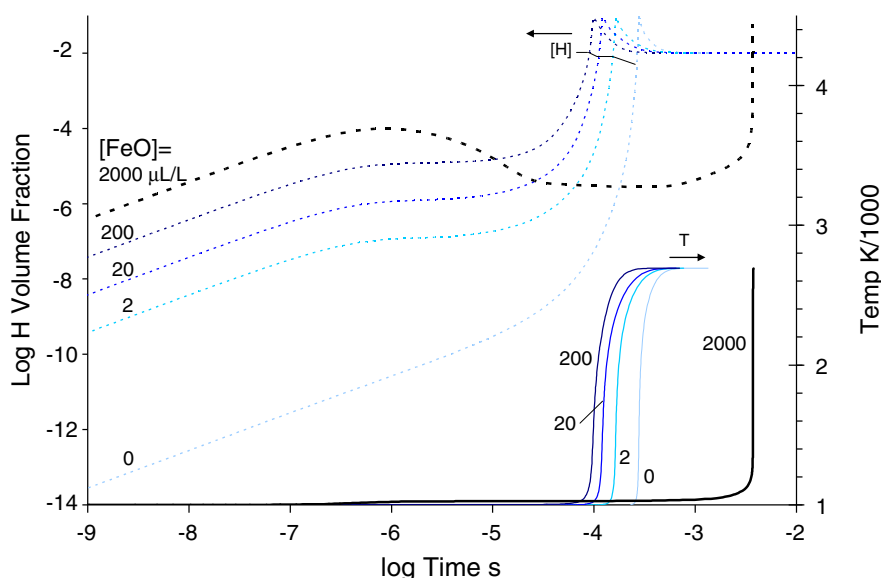


Fig. 3. H volume fraction (dotted curves, left scale) and temperature (solid curves, right scale) with time for H_2 -air system ($T = 1000$ K, $P = 1.01$ bar, $\phi = 1.0$) and FeO addition at (0, 2, 20, 200, and 2000) $\mu\text{L/L}$.

the equilibrium temperature is 2683 K with X_H about 0.01.

In Fig. 1, as the volume fraction of iron species increases, τ eventually increases sharply. To investigate the cause, we examine the species concentrations and reaction fluxes at $X_{\text{FeO}} = 1400$ $\mu\text{L/L}$. At that condition, the catalytic radical recombination cycles (see Fig. 2c) are responsible for 42% of the H atom consumption and 18% of the O atom consumption, and a negligible amount of radical formation. That is, as the radical pool increases to the typical super-equilibrium levels, the gas-phase radical recombination cycles act to reduce radical concentrations, just as they did in the inhibition of laminar premixed and diffusion flames by the iron compounds.

An important feature of the flame inhibition mechanism by iron containing additives is the regeneration of the intermediate active species (Fe, FeO, FeOH, FeO₂, and Fe(OH)₂), so that catalytic cycles exist (as illustrated in Fig. 2c) which lead to a substantially increased overall recombination rate of chain carriers. While such cycles can, in principle, run backwards to create radicals [18,33] (and thereby greatly promote ignition), that is not the case for the present conditions. As described above, FeO₂ (at early times) is a sink for the iron species, and no reactions are fast enough to consume it. This is illustrated in Fig. 2a and b, which show that FeO₂ has no significant consumption path, due largely to thermodynamic constraints on the metal species concentrations [34], and partly on the low levels of H atom at early times. Thus, acceleration of the initial reaction is related to an additional radical source due to additive decomposition, and does not involve catalytic cycling reactions. To some extent the level of the promotion is proportional

to the amount of additive, and the increase in the radical pool at the initial stage does not exceed the initial added concentration of iron-containing species. On the other hand, metals may exist for which the intermediate species have different thermodynamic properties so that compete cycles might exist for ignition promotion. This is the case for HBr, for which a reaction cycle involving HBr and HO₂ promotes H_2 -O₂ ignition [17,18].

It should be noted that reaction of metal-containing species with HO₂ (chain de-branching reactions, (1)–(4) above), which were suggested to describe suppression of engine knock by lead in hydrocarbon-air systems [31], were not found to make a contribution to the reaction process for the conditions in the present paper, (i.e., τ with and without the HO₂ reactions (1)–(4) above differed by less than 1%). The reason is that the iron inhibition reactions (Fig. 2c) become important only when the radical volume fractions get high, by which time the HO₂ concentration is starting to be reduced by its reaction with radicals, so that HO₂ catalytic cycles are less important than those of H and O in Fig. 2c.

While the higher iron species volume fractions shown in Fig. 1 are likely to represent super-saturated conditions at $T = 1000$ K [2], rate limitations to the condensation processes are likely to limit loss of the iron compounds to particle formation in the short times during which the promotion occurs (≈ 1 μs) [35]. Hence, the promotion reactions, even at high iron loading, are likely to be relevant. On the other hand, for the inhibition reactions, their much longer time scales would make the system vulnerable to vapor-pressure limitations for the active iron species, and condensation of iron species may limit the inhibition of ignition.

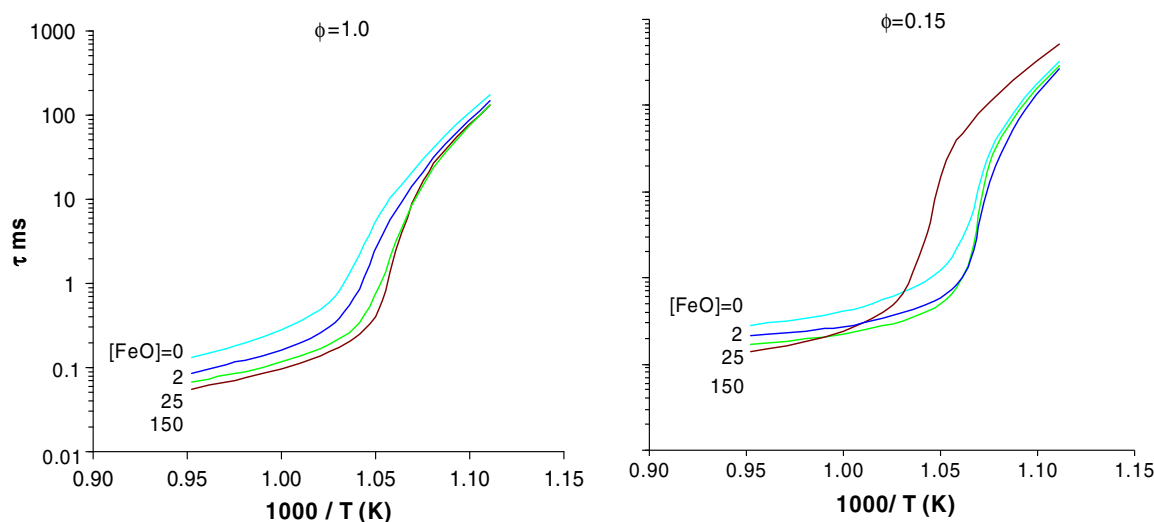


Fig. 4. Calculated ignition delay τ (H_2 -air, $P = 1$ bar) with FeO added at (0, 2, 25, and 150) $\mu\text{L/L}$ at $\phi = 1.0$ (left) or $\phi = 0.15$ (right) as a function of initial temperature.

The ignition delay τ was also calculated for $\phi = 0.15, 0.25, 0.75,$ and 1.0 , with FeO or $\text{Fe}(\text{CO})_5$ from $0 \mu\text{L/L}$ to $150 \mu\text{L/L}$ (not shown here). For the pure H_2 -air case (no added iron compound), τ is relatively constant for $0.25 \leq \phi \leq 1.0$, and a minimum ignition delay is predicted to occur at fuel-lean conditions near $\phi = 0.75$, while near the lean flammability limit, τ increases rapidly. With FeO addition, τ decreases, but the variation with ϕ is qualitatively the same as in the neat case.

The modeling results demonstrate that the promotion effect is larger in the lean hydrogen/air mixtures. As the curves for FeO and $\text{Fe}(\text{CO})_5$ in Fig. 1 show, the absolute decrease in τ as X_a increases is somewhat larger for $\phi = 0.15$ than for 1.0 , for either FeO or $\text{Fe}(\text{CO})_5$ addition (but since the value of τ is higher for $\phi = 0.15$, the fractional decrease in τ is less as either FeO or $\text{Fe}(\text{CO})_5$ is added to the leaner mixtures). For the leaner conditions, the rapid increase in τ for X_a above around $100 \mu\text{L/L}$ occurs at a lower value of X_a . Analysis of the species volume fractions and reaction fluxes indicates that the mechanism of FeO's ignition promotion is modified in leaner mixtures. With lower initial $[\text{H}_2]$ for the leaner initial conditions, the relative rate of $\text{FeO} + \text{O}_2$ is higher as compared to $\text{FeO} + \text{H}_2$. Hence, in the leaner mixtures, the fraction of FeO reacting with O_2 ($\text{FeO} + \text{O}_2 \Rightarrow \text{FeO}_2 + \text{O}$) instead of H_2 (mostly $\text{FeO} + \text{H}_2 \Rightarrow \text{Fe} + \text{H}_2\text{O}$) is about seven times higher than in the stoichiometric mixtures. As a result, O atom is formed much earlier, and its branching reaction with H_2 ($\text{O} + \text{H}_2 \Rightarrow \text{O} + \text{OH}$) leads to higher radical pool concentrations earlier. This is illustrated in Fig. 1 (right frame), in which the effect of adding FeO in this mixture is equivalent to adding $[\text{H}]/1.5$, so that compared to the $\phi = 1.0$ condition, FeO is a much stronger promoter (although ignition is much more difficult to initiate at $\phi = 0.15$).

The effect of the initial temperature on the ignition delay in an H_2 -air system is shown in Fig. 4 for $\phi = 1.0$ (left frame) and $\phi = 0.15$ (right frame) with FeO added at (0, 2, 25, and 150) $\mu\text{L/L}$. For no FeO addition, the behavior changes dramatically around 960 K, so that between 925 and 980 K, the ignition delay decreases by about 60 times for $\phi = 1.0$, and 50 times for $\phi = 0.15$. As FeO is added, the ignition delay time is decreased, and the temperature at which the large reduction occurs is also reduced. Analysis of the reaction fluxes for 25 $\mu\text{L/L}$ of FeO, $\phi = 1.0$, and initial temperatures of 910 K and 980 K indicates that at the higher temperature, the reactions responsible for the early addition of radicals: $\text{FeO} + \text{H}_2 \Rightarrow \text{FeOH} + \text{H}$ and $\text{FeO} + \text{O}_2 \Rightarrow \text{FeO}_2 + \text{O}$, are 80% and 100% faster, respectively, than at the lower temperature. This explains why the promotion effects are larger at the higher temperature (as indicated in Fig. 4). Hence, addition of FeO is expected to make H_2 -air ignition occur at lower temperatures.

5. Concluding remarks

The potential for ignition promotion by trace iron compounds has been investigated through ignition delay calculations for atmospheric pressure H_2 -air mixtures near 1000 K. Calculations for a range of equivalence ratio and additive volume fraction have shown that small amounts ($\approx 1 \mu\text{L/L}$) of iron additives can reduce the ignition delay significantly ($\approx 33\%$), with peak reductions of a factor of two or three, near $50 \mu\text{L/L}$; a noticeable reduction ($\approx 1\%$) in the ignition delay is realized at an additive volume fraction of only 1×10^{-9} . The form of the iron has a large effect on the promotion action, with FeO the most effective moiety tested. The promotion occurs from

reactions of the iron compounds with H_2 or O_2 , which lead to radicals (H, O, or OH) at early times, which then accelerate the subsequent build-up of HO_2 in the system. For low additive volume fractions ($<10 \mu\text{L/L}$), FeO addition is equivalent to directly adding H atoms, reduced by a factor of fourteen, for $\phi = 1.0$, or reduced by a factor of about two for $\phi = 0.15$. Unlike flame inhibition, for which the iron-containing species form a catalytic cycle, the promotion reactions (for $50 \mu\text{L/L}$ of additive) occur through a direct chain sequence (since FeO_2 is a sink for iron species until the radical pool builds up). In addition to lowering the ignition delay, the iron compounds also lowered the cut-off temperature above which rapid ignition occurred. Above $\approx 100 \mu\text{L/L}$ of additive, the iron compounds inhibit ignition, and the mechanism is similar to the gas-phase catalytic radical recombination cycles found to be important in laminar premixed and diffusion flame inhibition by iron compounds. The switch from promotion to inhibition of the ignition occurs as the radical concentrations build-up fast enough (due to inhibitor breakdown) to allow FeO_2 to be consumed by O-atom attack, creating complete catalytic radical recombination cycles which are then stronger than the promotion.

The inhibition mechanism involving HO_2 is not important for the present conditions because promotion occurs at very early times (when HO_2 concentrations are small), and inhibition occurs at very late times, when the main radical pool has built up, so that reactions of iron species with the main chain branching radicals (H, O, and OH) are much faster than with HO_2 . At intermediate times, the reactions of iron species with HO_2 are low because they are both present at low concentrations.

The results of present work demonstrate that highly effective flame inhibitor additives (fire suppressants) can have a promotion or inhibition effect on the ignition processes depending on the initial conditions. The promotion effect is the result of relatively fast delivery of active intermediate species during radical pool build-up, which increases the reaction rate and decreases the ignition delay.

Acknowledgment

The authors are grateful to Prof. Forman Williams for suggesting the present investigation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2008.09.006.

References

- [1] V.I. Babushok, W. Tsang, *Combust. Flame* 123 (4) (2000) 488–506.
- [2] D. Reinelt, G.T. Linteris, *Proc. Combust. Inst.* 26 (1996) 1421–1428.
- [3] D.H. Cotton, D.R. Jenkins, *Trans. Faraday Soc.* 67 (1971) 730–739.
- [4] K. Park, G.T. Bae, K.S. Shin, *Bull. Korean Chem. Soc.* 23 (2) (2002) 175–176.
- [5] K.S. Shin, *Bull. Korean Chem. Soc.* 25 (5) (2004) 745–746.
- [6] J.E. Dolan, P.B. Dempster, *J. Appl. Chem.* 5 (1955) 510–517.
- [7] M.E. Morrison, K. Scheller, *Combust. Flame* 18 (1972) 3–12.
- [8] K.H.L. Erhard, R.G.W. Norrish, *Proc. Royal Soc. Lond. A* 234 (1956) 178–191.
- [9] S. Matsuda, D. Gutman, *J. Phys. Chem.* 75 (15) (1971) 2402–2404.
- [10] S. Matsuda, *J. Phys. Chem.* 57 (2) (1972) 807–812.
- [11] A. Davis, D.E. Hoare, A.D. Walsh, *Proc. Combust. Inst.* 13 (1971) 63–71.
- [12] J.W. Armitage, P. Gray, *Combust. Flame* 9 (2) (1965) 173–184.
- [13] P.G. Ashmore, B.J. Tyler, *Proc. Combust. Inst.* 9 (1963) 201–209.
- [14] P.G. Ashmore, B.P. Levitt, *Proc. Combust. Inst.* 7 (1959) 45–52.
- [15] F.E. Scott, R.W. VanDolah, M.G. Zabetakis, *Proc. Combust. Inst.* 6 (1956) 540–545.
- [16] D.R. Blackmore, G. O'Donnell, R.F. Simmons, *Proc. Combust. Inst.* 10 (1965) 303–310.
- [17] L.A. Lovachev, V.T. Gontkovskaya, N.I. Ozerkovskaya, *Combust. Sci. Technol.* 17 (3–4) (1977) 143–151.
- [18] L.A. Lovachev, L.N. Lovachev, *Combust. Sci. Technol.* 18 (5–6) (1978) 191–198.
- [19] I.O. Moen, P.A. Thibault, J.H. Lee, R. Knystautas, T. Dean, C.K. Westbrook, *Proc. Combust. Inst.* 20 (2008) 1717–1725.
- [20] V.I. Babushok, D.R.F. Burgess, W. Tsang, A.W. Miziolek, in: *Halon Replacements*, 1995, pp. 275–288.
- [21] W.L. Grosshandler, G.W. Gmurczyk, in: Y. Haseemi (Ed.), *tl. Association for Fire Safety Science*, Boston, MA, 1997, pp. 853–864.
- [22] SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics With Sensitivity Analysis, SAND87-8248, Sandia National Laboratories, Livermore, CA, 1988.
- [23] CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics, SAND89-8009B, Sandia National Laboratories, Livermore, CA, 1989.
- [24] D.R. Burgess, in: *XSenkplot*, an interactive, graphics postprocessor for numerical simulations of chemical kinetics, available at <http://www.nist.gov/cstl/div836/xsenkplot>, (National Institute of Standards and Technology, Gaithersburg, MD, 1997).
- [25] G.T. Linteris, M.D. Rumminger, V.I. Babushok, *Combust. Flame* 122 (1–2) (2000) 58–75.
- [26] M.T. Allen, R.A. Yetter, F.L. Dryer, *Combust. Flame* 109 (1997) 449–470.
- [27] T.J. Kim, R.A. Yetter, F.L. Dryer, *Proc. Combust. Inst.* 25 (1994) 759–766.

- [28] M.D. Rumminger, D. Reinelt, V.I. Babushok, G.T. Linteris, *Combust. Flame* 116 (1–2) (1999) 207–219.
- [29] M.D. Rumminger, G.T. Linteris, *Combust. Flame* 120 (4) (2000) 451–464.
- [30] M.D. Linteris, G.T. Rumminger, in: L. Michel Curtat (Ed.), *International Association for Fire Safety Science*, Marne-La-Vallee, France, 2000, pp. 289–300.
- [31] S. Benson, *J. Phys. Chem.* 92 (1988) 1531–1533.
- [32] W.J. Pitz, C.K. Westbrook, *Combust. Flame* 63 (1–2) (1986) 113–133.
- [33] D.H. Cotton, N.J. Friswell, D.R. Jenkins, *Combust. Flame* 17 (1971) 87–98.
- [34] G.T. Linteris, V.R. Katta, F. Takahashi, *Combust. Flame* 138 (1–2) (2004) 78–96.
- [35] M.D. Rumminger, G.T. Linteris, *Combust. Flame* 128 (1/2) (2002) 145–164.