# The Inhibition Effect of Fe(CO)$_5$ on the Ignition of Ethane

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Halons (halocarbons) have been employed extensively as fire suppression agents over the past three decades, but now have been phased out due to indications they may be responsible for the depletion of stratospheric ozone.[1] As a result, efficient, nontoxic flame suppression agents must be found to replace halons. Obvious alternatives are other halogenated hydrocarbons, and much research has recently been devoted to understanding their relative performance and inhibition mechanisms.[2] However, an agent with all of the desired properties of CF$_3$Br (halon 1301) is proving difficult to find. Consequently, additional research is necessary to identify new suppressants and understand the mechanisms of inhibition of known, effective agents.

Flame studies have shown that metal-containing compounds are promising candidates for replacing halons as fire suppression agents.[3] In particular, flame velocity studies indicate Fe(CO)$_5$ can be up to sixty times more efficient a flame inhibitor than CF$_3$Br.[3] Little has been known, however, about the kinetic mechanism by which iron achieves such impressive flame inhibition. Although iron pentacarbonyl itself is too toxic to be a useful halon replacement, understanding the reasons for its efficiency could provide valuable insight into which chemical properties are most critical to efficient flame inhibition.

The first experimental studies of flame inhibition by iron pentacarbonyl are the studies of Wagner and co-workers[4,5] The inhibition effect of Fe(CO)$_5$ was investigated by measuring the burning velocity of premixed flames with inhibitor added to the reactants. In that research, Bonne *et al.*[5] found Fe(CO)$_5$ to be significantly more effective than Br$_2$ in premixed H$_2$-air and hexane-air flames and found that its inhibition effectiveness decreased as the pressure was reduced below atmospheric. Reinelt and Linteris[6] studied the flame inhibition effect of iron pentacarbonyl in premixed flames by measuring the burning velocity, and in counterflow diffusion flames by measuring the extinction strain rate. They found that at low Fe(CO)$_5$ mole fraction, the burning velocity was strongly dependent on inhibitor mole fraction, whereas at high Fe(CO)$_5$ mole fraction, the burning velocity was nearly independent of inhibitor mole fraction.

In our previous work,[7] it was found that the small amount of Fe(CO)$_5$ did not cause an increase in the ignition delay of methane. It was a quite surprising result, because that was attempted to increase the ignition delay of methane by addition of Fe(CO)$_5$ which was known to decrease flame velocity of hydrocarbons effectively. In the present work, the addition effect of Fe(CO)$_5$ on C$_2$H$_6$ ignition was investigated in order to understand the general features of Fe(CO)$_5$ as a combustion inhibitor. The characteristics of the oxidation of CH$_4$ are different from all other hydrocarbons. The dissociation energy of the C-H bond in CH$_4$ (435 kJ/mol) is much higher that of C-C bonds in C$_2$H$_6$ (370 kJ/mol) or larger aliphatics.[8] For this reason, the oxidation of ethane can be a model paradigm for the study of the combustion of all aliphatic hydrocarbons.

## Experimental Section

The experiments were done utilizing reflected shock waves in a Monel shock tube of 7.62 cm inside diameter which was described in detail elsewhere.[9-11] Shock parameters were computed from measured incident shock velocities by standard methods[12] under the assumption of steady flow and no wall boundary layer formation. The ignition was measured by the sudden increase of pressure profile and OH emission intensity. The pressure measurements were made using a pressure transducer (Kistler 211B) which was located at the center of the end plate of the driven section. The transducer signal was amplified by a Kistler 504E amplifier and recorded using a digital oscilloscope (LeCroy 9304A). The characteristic ultraviolet emission from OH radical species at 306.7 nm was monitored using a photomultiplier tube (EMI 9924QB) with a band path filter through the sapphire window which was mounted flush at 2.7 cm from the end plate of shock tube. The compositions of the mixtures used in this work are given in Table 1. C$_2$H$_6$ (99.97%, Matheson), O$_2$ (99.997%, Matheson), Ar (99.999 %, Wilson) He (99.995%, Matheson) and Fe(CO)$_5$ (99.999 % Aldrich) were used without further purification. Test gas mixtures were prepared manometrically and allowed to stand for 48 hours before use. Using conventional reflected shock techniques, we measured ignition delay times by the sudden increase of pressure and OH emission in stoichiometric C$_2$H$_6$-O$_2$-Ar mixtures containing small amount of Fe(CO)$_5$.

**Table 1**. Experimental conditions

| | Compositions (%) | | | | $\tau$ ($\mu$s) | T$_5$ (K) |
|---|---|---|---|---|---|---|
| | C$_2$H$_6$ | O$_2$ | Fe(CO)$_5$ | Ar | | |
| Mixture 1 | 2.0 | 7.0 | – | 91.0 | 28-977 | 1218-1576 |
| Mixture 2 | 2.0 | 7.0 | 0.10 | 90.9 | 115-942 | 1231-1682 |
| Mixture 3 | 2.0 | 7.0 | 0.20 | 90.8 | 39-1298 | 1249-1424 |

## Results and Discussion

The ignition delay time ($\tau$) was defined as the time interval between the arrival of the reflected shock wave front and the onset of an ignition.[7] In Figure 1 the $\tau$ values are plotted logarithmically as a function of inverse temperature for all mixtures studied. The points are the observed values and the lines are least square fits to the data. A correlation between ignition delay and $Fe(CO)_5$ concentration was customarily summarized in the form of mass-action expression with an Arrhenius temperature dependence.[13] Multiple regression analysis was employed to obtain the best-fit parameters. This procedure gave

$$\tau = 6.54 \times 10^{-2} \exp (36.7 \text{ kcal mol}^{-1}/RT)$$
$$\times [Fe(CO)_5]^{0.32} (\text{mol/cm}^3)^{-0.32} \text{ sec}$$

where the ignition delay time $\tau$ and the concentration are given in sec and $\text{mol/cm}^3$, respectively. The reliability of this empirical formula was tested by plotting all data as $\log(\tau/$
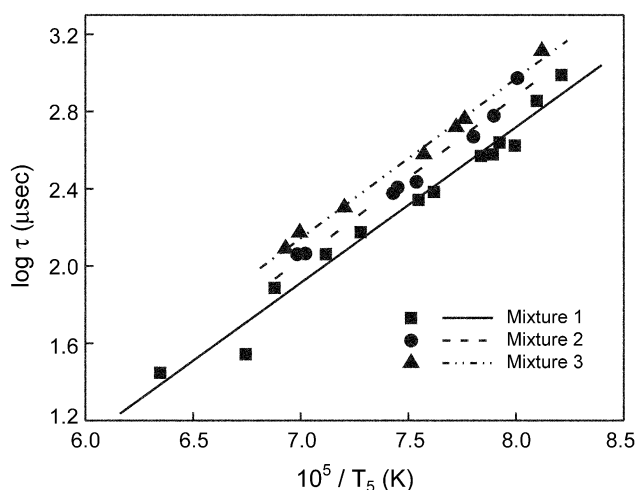


**Figure 1**. Ignition delay times for the mixtures in Table 1. Lines represent the least square fits for the corresponding mixtures using the expression in the text.
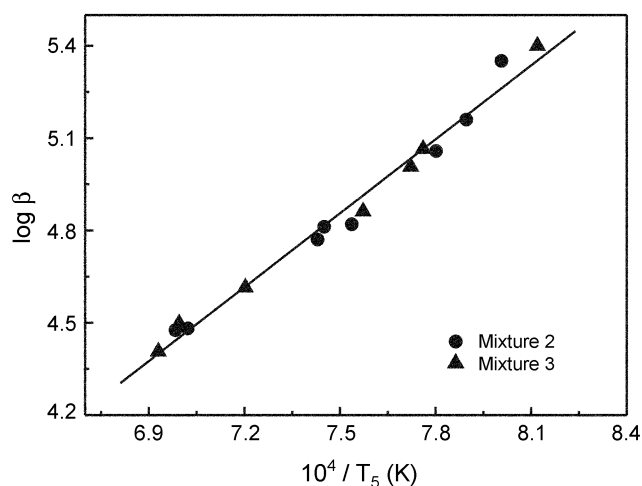


**Figure 2.** A plot of log ($\tau/[Fe(CO)_5]^{0.32}$) *vs.* $10^4/T_5$ for mixtures 2 and 3. The solid line represents the best fit for the mixtures.

$[Fe(CO)_5]^{0.32}$) *vs.* $10^4/T$. As shown in Figure 2, all points lie close to a single line. The power dependence of $Fe(CO)_5$ indicates the inhibiting effect; the ignition delay time increases by increasing the concentration of $Fe(CO)_5$.

In our previous work,[7] it was found that the small amount of $Fe(CO)_5$ promoted slightly the ignition of $CH_4$. This investigation, however, shows that the same amount of $Fe(CO)_5$ inhibits considerably the ignition of $C_2H_6$. The addition effects of $Fe(CO)_5$ on methane or ethane ignition are quite similar to those of $CH_3Cl$ or $CH_3Br$.[14-16] In case of the inhibition by $CH_3Cl$ on ethane ignition, the elementary reactions primarily responsible for suppressing ignition are $C_2H_6 + Cl \rightarrow C_2H_5 + HCl$ and $HCl + H \rightarrow Cl + H_2$. The removal of H atoms occurs as a result of these reactions, for their sum is just $C_2H_6 + H \rightarrow C_2H_5 + H_2$. Thus, these reactions compete with the chain branching reaction $H + O_2 \rightarrow OH + O$ for hydrogen atoms. The inhibiting effect of metal-containing species on ignition is more complicated. A chemical interpretation of flame inhibiting effect of $Fe(CO)_5$ has been developed by Rumminger *et al.*[17,18] on the basis of burning velocity measurements on $CH_4$-$O_2$-$N_2$ and $H_2$-CO-$O_2$-$N_2$ premixed and counterflow flames of varying composition. They report that their kinetic simulations agree with experimental observation for low concentration of $Fe(CO)_5$ but overpredict the flame inhibition at high concentrations.

In order to understand more details on the role of $Fe(CO)_5$ in methane or ethane ignition, numerical modeling study using the detailed reaction mechanism is needed to account for these observations.

### References

1. Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.
2. Miziolek, A. W.; Tsang, W. *Halon Replacements Technology and Science*; ACS Symposium Series 611: Washington, D. C., 1995.
3. Babushock, V.; Tsang, W. *Combust. Flame* **2000**, *123*, 488.
4. Jost, W.; Bonne, U.; Wagner, H. G. *Chem. Eng. News* **1961**, *39*, 76.
5. Bonne, U.; Jost, W.; Wagner, H. G. *Fire Res. Abstracts Rev.* **1962**, *4*, 6.
6. Reinelt, D.; Linteris, G. T. *26th Symposium (international) on Combustion*; The Combustion Institute: Pittsburgh, 1996; p 1421.
7. Park, K.; Bae, G. T.; Shin, K. S. *Bull. Korean Chem. Soc.* **2002**, *23*, 175.
8. Peterson, K. A.; Dunning, Jr. T. H. *J. Chem. Phys.* **1997**, *106*, 4119.
9. Baeck, H. J.; Shin, K. S.; Yang, H.; Qin, Z.; Lissianski, V.; Gardiner, Jr. W. C. *J. Phys. Chem.* **1995**, *99*, 15925.
10. Qin, Z.; Yang, H.; Lissianski, V.; Gardiner, Jr. W. C.; Shin, K. S. *Chem. Phys. Letters* **1997**, *276*, 110.
11. Shin, K. S.; Yoo, S. J. *Bull. Korean Chem. Soc.* **2004**, *25*, 293.
12. Gardiner, Jr. W. C.; Walker, B. F.; Wakefield, C. B. In *Shock Waves in Chemistry*; Lifshitz, A. Ed.; Marcel Dekker: New York, 1981; p 319.
13. Tsang, W.; Lifshitz, A. *Annu. Rev. Phys. Chem.* **1990**, *41*, 559.
14. Shin, K. S.; Kang, W. K.; Shim, S. B.; Jee, S. B. *J. Korean Chem. Soc.* **1999**, *43*, 150.
15. Shin, K. S.; Park, K.; Kim, K. *Bull. Korean Chem. Soc.* **2001**, *22*, 330.
16. Jee, S. B.; Kim, K.; Shin, K. S. *Bull. Korean Chem. Soc.* **2000**, *21*, 1015.
17. Rumminger, M. D.; Reinelt, D.; Babushok, V.; Linteris, G. T. *Combust. Flame* **1999**, *116*, 207.
18. Rumminger, M. D.; Linteris, G. T. *Combust. Flame* **2000**, *120*, 451.