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Communications

The Addition Effect of $Fe(CO)_5$ on Methane Ignition

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It has been shown that methane has the longest ignition delay time among the simple aliphatic hydrocarbons.[1-3] This phenomenon can be explained by the fact that the C-H bond in methane is considerably stronger than the C-C bond in larger hydrocarbons.[2] It was also shown that by adding small amounts of ethane or propane to methane, it was possible to shorten its ignition delay time.[4] Whereas it is rather simple to shorten the ignition delay of methane, we are not aware of any attempt to increase its delay.

Recently, flame studies have shown that metal-containing compounds are promising candidates for replacing halons as fire suppression agents. In particular, flame velocity studies indicate that $Fe(CO)_5$ can be up to sixty times more efficient a flame inhibitor than CF_3Br.[5] 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. A chemical interpretation of flame inhibiting effect of $Fe(CO)_5$ has been developed by Rumminger *et al.*[7,8] 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.

Up to date, most of the works on the flame inhibition by iron pentacarbonyl have been done by measuring the burning velocity in flames. Therefore, we undertook to charac-

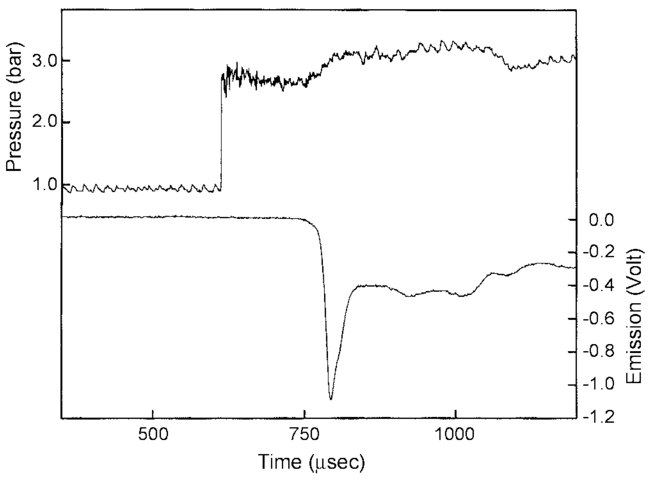

Figure 1. Typical experimental record showing pressure (upper) and OH emission (lower). Experimental conditions were P_1=54 torr and T_5=1763 K in mixture 3.

Table 1. Experimental condition

	CH_4 (%)	O_2 (%)	$Fe(CO)_5$ (%)	Ar (%)	(s)	T_5 (K)
Mixture 1	2.0	4.0	–	94.00	97-1134	1616-2011
Mixture 2	2.0	4.0	0.05	93.95	85-1056	1591-2012
Mixture 3	2.0	4.0	0.10	93.90	110-1065	1599-1864
Mixture 4	2.0	4.0	0.20	93.80	148-961	1611-1834

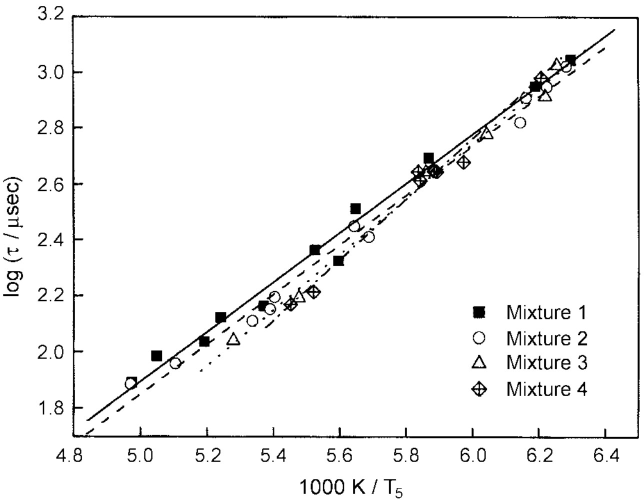

Figure 2. Ignition delay times for the mixtures in Table 1. Lines indicate linear fit for each mixtures.

terize the influence of low levels of $Fe(CO)_5$ on the ignition of methane.

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.[9,10] Shock parameters were computed from measured incident shock velocities by standard methods[11] 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. CH_4 (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.

A typical pressure record showing the shock heating and the ignition phenomenon is shown in Figure 1. The ignition delay time (τ) was defined as the time interval between the arrival of the reflected shock wave front and the onset of an ignition. In Figure 2 the τ 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. The temperature dependence on the ignition of mixtures 1-4 are different. At high temperature the concentration dependence of $Fe(CO)_5$ is obvious, while at low temperature the dependence of $Fe(CO)_5$ is unclear. These experimental data can be expressed by the least-square method as follows:

$$\tau/\mu s = 2.95\times10^{-3} \exp(2.03\times10^4 \text{ K}/T_5) \quad \text{for mixture 1,}$$
$$\tau/\mu s = 2.40\times10^{-3} \exp(2.05\times10^4 \text{ K}/T_5) \quad \text{for mixture 2,}$$
$$\tau/\mu s = 4.47\times10^{-4} \exp(2.34\times10^4 \text{ K}/T_5) \quad \text{for mixture 3,}$$

and

$$\tau/\mu s = 1.74\times10^{-4} \exp(2.50\times10^4 \text{ K}/T_5) \quad \text{for mixture 4.}$$

The slopes of the mixtures 1-4 increase as the concentration of $Fe(CO)_5$ increases, indicating that the promotion effect at high temperature is larger than that at low temperature. As can be seen in Figure 2, none of the mixtures including $Fe(CO)_5$ caused an increase in the ignition delay of methane. On the contrary, all the data points scatter slightly below the points of pure methane, indicating that a promotion effect which shortens the ignition is obtained. It was quite surprising result, because this investigation 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. This investigation, however, shows that the addition of small amount of $Fe(CO)_5$ rather promotes the ignition of methane than retards it.

Numerical modeling study using the detailed reaction mechanism is needed to account for the observations. A reliable reaction mechanism with the rate constants of each elementary steps as well as the thermochemical data for the iron containing species are under investigation in our laboratory.

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