IRON PENTACARBONYL IN CH_4 - O_2 AND AIR FLAMES

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Investigating the influence of additives on the propagation velocity and other flame characteristics of laminar flames we tested several substances which showed very pronounced effects on the propagation velocity. One of these was $Fe(CO)_5$.

In the course of our investigations of reaction rate in low-pressured flames we tried to find the mode of action of $Fe(CO)_5$ in hydrocarbon-air and hydrocarbon-oxygen flames. To this purpose the pressure dependence of the influence of $Fe(CO)_5$ was first investigated. In fig. 1 the burning speeds (λ)x of methane oxygen mixtures are shown as function of composition. Contrary to other observations (including our own with carbon-monoxide in mixtures with oxygen) but in agreement with our measurements with C_2H_4 and C_2H_6 the burning speed is practically independent of pressure (near the value of maximum flame velocity) down to pressures of about 1 at. Below 0.1 at. the flame speed starts to increase with decreasing pressure.

Fig. 2 gives the influence of iron pentacarbonyl on the burning speed of the stoichiometric CH_4-O_2 mixtures at the corresponding pressures. (The $Fe(CO)_5$ concentration is given in volume percent of the whole mixture). Small inhibitor concentrations have a distinct, but not strong influence. The influence decreases with decreasing pressure (the $Fe(CO)_5$ concentration is proportional with pressure). In methane-air mixtures (fig. 3) (as well as in other hydrocarbon-air mixtures) the influence of $Fe(CO)_5$ is much more pronounced. 0.01 % of $Fe(CO)_5$ causes a decrease in burning speed by 25 % at atmospheric pressure. If one compares the influence of $Fe(CO)_5$ not in volume percent of the total mixture but in volume percent of the fuel it still remains three times more active in mixtures with air than in those with oxygen. As in CH_4-oxygen mixtures the additive becomes less active with decreasing pressure. This still holds if the absolute $Fe(CO)_5$ concentration in molecules per cm^3 remains the same. For comparison fig. 4 shows the influence of added bromine and iron pentacarbonyl on the burning speeds of hydrogen-air (37% H_2) and stoichiometric n-hexane air, for higher percentages of added bromine and chlorine. As was to be expected, the influence of bromine is stronger than that of chlorine, and, less easily expected, benzene is more susceptible to the action of additives than hexane. The effectiveness of $Fe(CO)_5$ in every case is much more pronounced than that of the halogenes and halogenated hydro-carbons.

x
$(\lambda^* = [O_2]/[O_2]_{stoich})$

Though the influence of $Fe(CO)_5$ markedly decreases with decreasing pressure the investigation of the action of this additive on low-pressure flat flames seemed to be useful for learning something about the specific action of the inhibitor on the chemical reaction. The following results may be considered as preliminary ones.
CH_4-air flames were investigated in some detail with and without additives. The flames were kept burning on flat-flame burners with 12 and 20 cms. diameter, mostly at 60 mm Hg pressure. Temperatures were measured by several independent methods: surface protected platinum-platinum-rhodium thermocouples with compensation for radiation losses, rotational temperatures of OH-bands and occasionally line reversal temperatures.

In fig. (6) the flame temperatures (thermocouple) is plotted versus distance above burner (centimeters) for three different mixtures (1.1 CH_4+10 air, CH_4+10 air, 0.9 CH_4+10 air) burning at 60 mm Hg with a burning speed v_n = 0.33 m/sec without additive. Flame temperature and burning speed under these circumstances, of course, depend on the flow conditions chosen. For comparison some rotational temperature values determined from the absorption spectrum of OH are plotted in the same curves.

With added $Fe(CO)_5$, 0.001 % by volume in the mixture, the thermocouple measurements are no longer reliable, due to iron oxide deposit. This changes radiation losses, and, in addition, may give rise to heterogeneous reactions. From former investigations there is no doubt, that OH radicals play an important role in the propagation of all flames of hydrogen containing compounds. In Fig. 8 OH-concentration and temperature for the stoichiometric CH_4-air flame are plotted as function of distance from the burner. The decrease of OH concentration in the "burned" gas is mainly due to diffusion losses. In fig. 9 the decrease of OH absorption (as measure for concentration, but not corrected for finite optical thickness) in the burned gases is plotted for the pure mixture of methane with air, for 0.001 % $Fe(CO)_5$ and 0.005 % $Fe(CO)_5$ added to the mixture. The concentration decrease of OH itself would be somewhat steeper. The initial increase in OH concentration and its maximum value are hardly influenced by added $Fe(CO)_5$. Only the position where OH absorption increases is shifted away from the burner with increasing $Fe(CO)_5$ concentration, and the flames become less stable. If one plots the logarithm of the OH concentration in the zone of nearly constant temperature, for flames with $Fe(CO)_5$ added, as function of the height above the burner, straight lines are obtained. This points to a decay reaction of first order in the radical concentration.

For very low $Fe(CO)_5$ concentrations the rate is proportional to the $Fe(CO)_5$ concentration, while for increasing $Fe(CO)_5$ concentration its relative influence seems to decrease.

From the experimental results obtained till now we cannot decide whether the recombination reaction of OH is homogeneous or heterogeneous, but it seems that at relatively high $Fe(CO)_5$ concentrations a heterogeneous decay reaction is dominant while at very low concentrations a homogeneous reaction may become important. In order to achieve further information, spectra of the flames were taken. (The middle of the flame was focused on the slit of the spectroscope). No. 1, in fig. 10 shows the emission of a stoichiometric CH_4-air flame at 60 mm Hg around the maximum of OH emission (0.1 - 0.9 cms. above the burner). No. 2 shows the emission of the same flame at 2.6 to 3.4 cms. above the burner. The Nos. 3-6 show emission spectra of the same flame, but with 0.005 % $Fe(CO)_5$ added. No. 3 represents the zone 0.1-0.9 cms. above the burner (two different exposure times).The exposure time of all spectra was identical, while in No. 4, 5, 6 the weaker spectra correspond to 1/15th of the normal exposure time. In the flames with $Fe(CO)_5$ iron lines and the emission of FeO is seen, but there is no pronounced continuous emission. In the following pictures the emission of different particles measured by a high resolution monochromator are plotted as function of the height above the burner. (fig. 11, 12, 14) As in other cases maximum emission of OH, maximum concentration of OH as well as maximum emission of C_2 and CH do not coincide at all. The emission maximum of OH may be linked to a maximum of reaction rate as the emission maxima of C_2, CH Fe and the first maximum of FeO. A measure for the concentration of iron atoms is given by fig. 14 where the absorption of the 3859.91 Å iron line is plotted for different $Fe(CO)_5$ concentrations, (see Fig. 13). While in the flame zone the emission of OH, C_2, CH and Fe has a pronounced maximum and then decreases very rapidly, the emission of FeO shows a different behavior. It has a second maximum about 3 cms above the burner, in a zone, where OH concentration and Fe absorption decrease rapidly. Then the intensity decreases in a zone where the temperature is still high. Fe,of course, forms solid particles in the flame, but the decrease in radiation intensity does not seem to be connected with the decay of FeO concentration but the second emission maximum of FeO, as well as the first one, seems to be due to chemiluminescence, to the decay of radicals in that zone.

The results, reported, concerning the investigation of the influence of $Fe(CO)_5$ (and other additives) on the reaction in low pressure flames were made to obtain first impression of the action of this very active inhibitor on the chemical reaction. The investigations are still in progress.

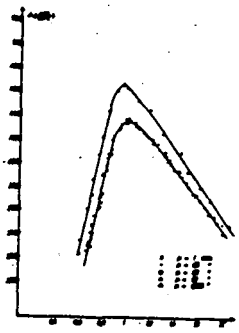

Fig.1 Influence of mixture composition and pressure on the flame velocity of CH_4-O_2-flames.

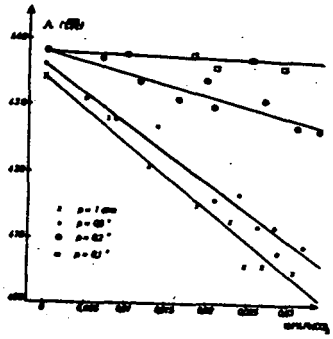

Fig.2 Influence of $Fe(CO)_5$ and pressure on flame velocity of stoich. CH_4-O_2-flames.

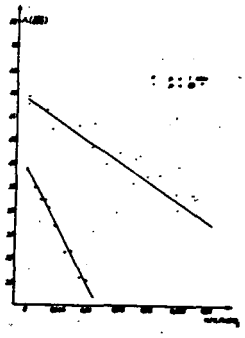

Fig.3 Influence of $Fe(CO)_5$ and pressure on the flame velocity of stoich. CH_4-air-flames.

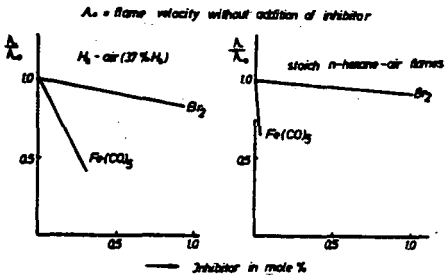

Fig.4 Influence of Br_2 and $Fe(CO)_5$ on the flame velocity.

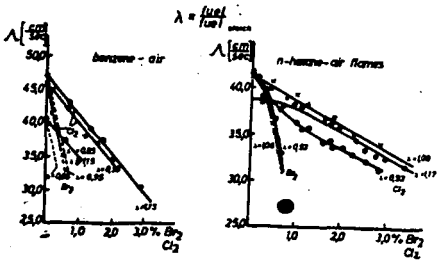

Fig.5 Influence of Br_2 and Cl_2 on the flame velocity.

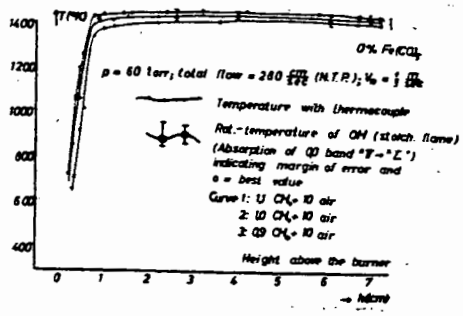

Fig. 6 Temperature in CH_4-air-flames (Pt-Pt 10% Rh-thermocouple)

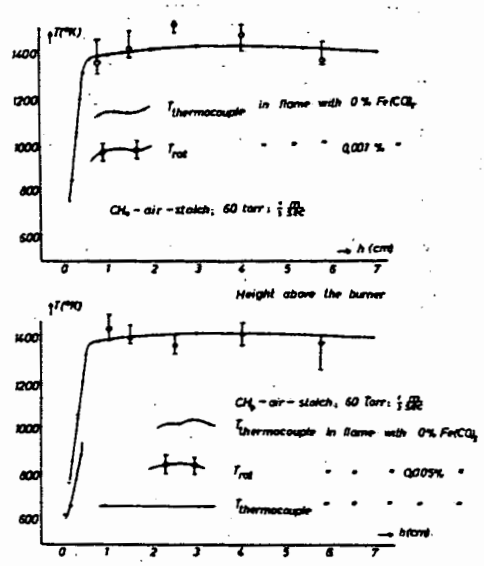

Fig. 7a, 7b Influence of $Fe(CO)_5$ on CH_4-air-flames
I. Comparison of temperatures.

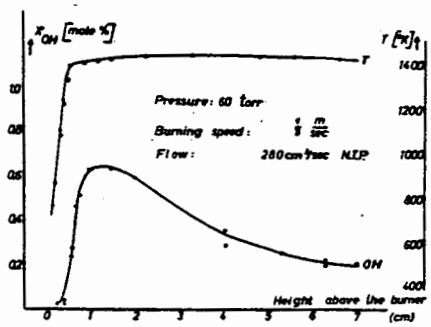

Fig. 8 Temperature and OH-concentration in a stoich. CH_4-air-flame without $Fe(CO)_5$.

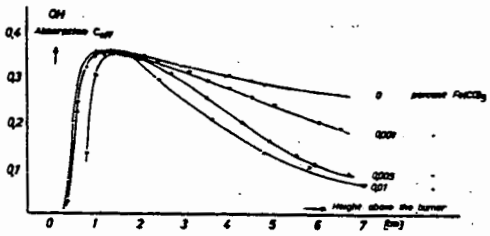

Fig. 9. Influence of $Fe(CO)_5$ on CH_4-air-flames.

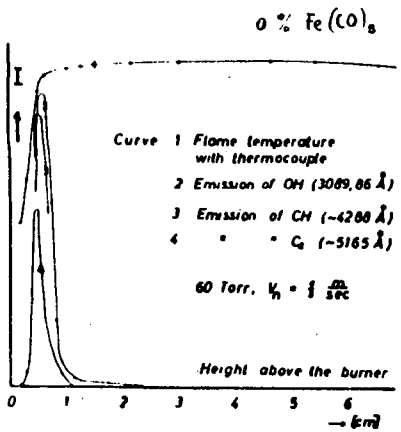

Fig.11 Influence of $Fe(CO)_5$ on stoich. CH_4-air-flames.

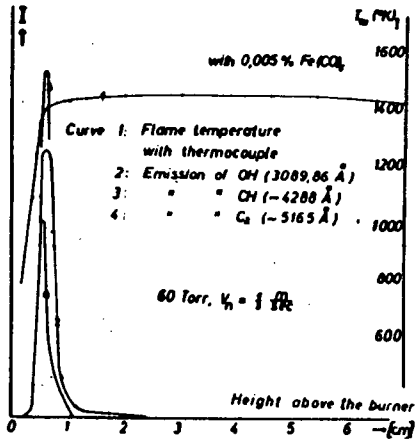

Fig.12 Influence of $Fe(CO)_5$ on stoich. CH_4-air-flames.

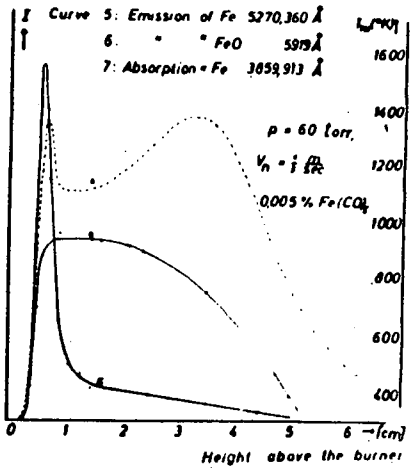

Fig.13 Influence of $Fe(CO)_5$ on CH_4-air-flames. Course of Fe and FeO.

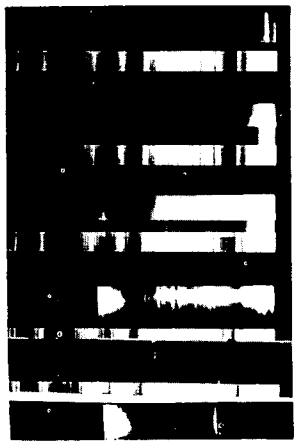

Fig. 10 Emission spectra

No.	Height above the burner		Remarks
6	6,0 - 6,8 cm	0.005 % $Fe(CO)_5$	FeO
5	3,1 - 3,9 "		max. of FeO Emission
4	1,1 - 1,9 "		
3	0,1 - 0,9 "		max. of OH Emission
2	2,6 - 3,4 "	0 "	
1	0,1 - 0,9 "		max of OH Emission

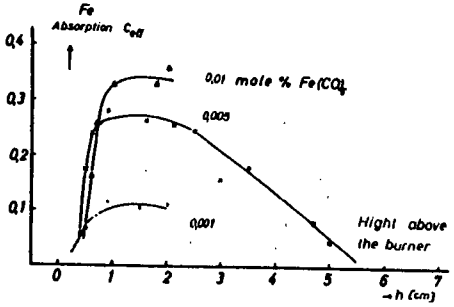

Fig. 14 Influence of $Fe(CO)_5$ on stoich. CH_4-air-flames Fe-concentration (C_{eff} of Fe 3859,913 A)