KURZE MITTEILUNGEN

Bis am 20. des Monats bei der Redaktion eingehende kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht
Es werden auch Manuskripte aus dem Auslande angenommen

The Effect of Iron Pentacarbonyl on Gas Phase Explosions*

A number of publications appeared over the last few years which considerably improved our understanding of the old problem of knock in spark ignition engines and of the action of anti-knock additives such as tetraethyl-lead (TEL). Most of the work was done with specially designed single and multi cylinder engines[1, 2] and rapid adiabatic compression machines,[3] but recently the technique of flash photolysis[4] was also successfully employed.[5, 6] The engine studies showed that the octane number of a fuel is uniquely coupled with the ignition delay of a fuel-air mixture where a low octane fuel has a short induction period and a high octane number results in a larger ignition delay.[2] From this it follows at once that an increase of the octane number by a suitable additive is achieved by delaying the point of the autoignition. This was proved experimentally and for TEL in particular it was shown that it is only effective when it decomposes at a time before the 'unleaded' fuel would otherwise ignite.[2]

Using an idealized system, ERHARD and NORRISH reinvestigated combustion reactions of a similar type.[5, 6] The explosions were initiated by the flash photolysis of a small concentration of aliphatic nitrites and the advancement of the combustion was followed by absorption as well as by emission spectroscopy. In this way ignition delays could be measured accurately because the explosion is associated with the appearance of relatively high concentrations of free radicals, such as OH, CH, C_2, CN and NH, whose absorption spectra could be readily photographed with the help of an electronically timed flash light source. It was also possible to observe the light emission of these radicals with a photomultiplier and to display the signal against time on a cathode ray oscilloscope. It was shown that on the addition of small concentrations of TEL the ignition delays were lengthened two to three times. During these extended induction periods the spectrum of gaseous diatomic lead monoxide was always observed showing that the decomposition of the TEL is followed by the rapid formation of PbO. Towards the end of the induction period the lead monoxide disappears and is replaced by atomic lead. These observations agree well with the engine experiments and provide detailed pictures at the same time.

There are, however, other compounds than TEL—containing manganese and iron—which also function as anti-knocks. The work on TEL of ERHARD and NORRISH[5, 6] was extended by CALLEAR and NORRISH[7, 8] and among many other additives ferrocene and iron pentacarbonyl were investigated. These authors report that neither of the two iron containing compounds affected the duration of the induction periods, under a wide variety of fuel compositions and flash energies, in spite of the fact that they are anti-knocks. CALLEAR and NORRISH also observed—probably for the first time—that the emission of the iron oxide spectrum occurs with extraordinary brilliance and they suggest that this intense light emission is the cause of a second anti-knock effect, functioning by radiative cooling or by removal of high potential chemical energy.

During the course of some work being done here similar experiments were performed with iron pentacarbonyl and an unexpectedly great influence on the ignition delay was observed. Iron pentacarbonyl can both lengthen and shorten the induction periods enormously. The effect depends very much on the concentration of the additive and markedly on the photolytic flash energy. Figure 1 shows the results which were obtained with an explosive mixture containing 1 mm (Hg) pentylnitrite + 30 mm hydrogen + 22 mm oxygen. It was ignited with two different photolytic flash energies, 675 Joules (°) and 1350 Joules (ˣ). With the lower flash energy the mixture responds very well to iron pentacarbonyl, since the induction period increases steadily up to 0.1 mm $Fe(CO)_5$. No explosions at all could be observed in the concentration range from 0.1 mm (Hg) to 0.4 mm of iron pentacarbonyl. From this point on the induction periods decrease again and become eventually shorter than the ignition delay of the original mixture. All the points of the graph were obtained by observing the light emission of the OH-radical and of the FeO band systems A and B. Both these emissions from quite different spectral regions occur at the same time but while the magni-

* Received June 24 th, 1961.

[1] B. M. STURGIS, *SAE Transactions 63* (1955) 253.
[2] E. B. RIFKIN and C. WALCUTT, *SAE Transactions 65* (1957) 552.
[3] C. F. TAYLOR, E. S. TAYLOR, J. C. LIVENGOOD, W. A. RUSSELL and W. A. LEARY, *SAE Transactions 4* (1950) 232.
[4] G. PORTER, *Proc. Roy. Soc. A 200* (1950) 284.
[5] K. H. L. ERHARD and R. G. W. NORRISH, *Proc. Roy. Soc. A 234* (1956) 178.
[6] K. H. L. ERHARD and R. G. W. NORRISH, *Proc. Roy. Soc. A 259* (1960) 297.
[7] A. B. CALLEAR and R. G. W. NORRISH, *Nature 184* (1959) 1794.
[8] A. B. CALLEAR and R. G. W. NORRISH, *Proc. Roy. Soc. A 259* (1960) 304.

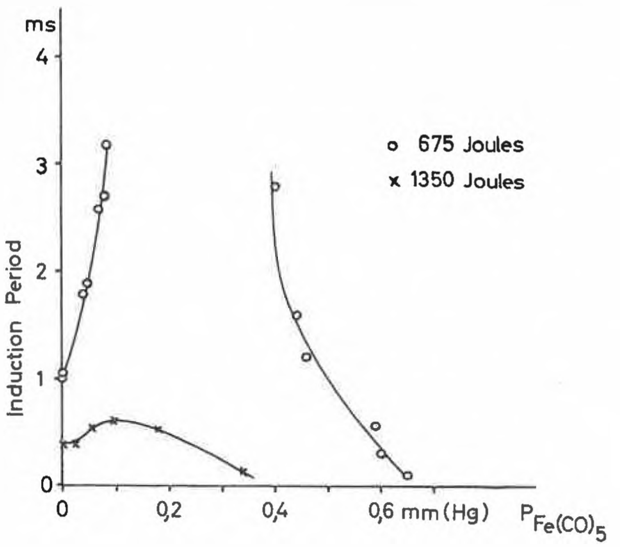

Fig. 1. The induction periods versus pressure of iron pentacarbonyl for two photolytic flash energies. – Mixture: 1 mm pentylnitrite + 30 mm hydrogen + 22 mm oxygen

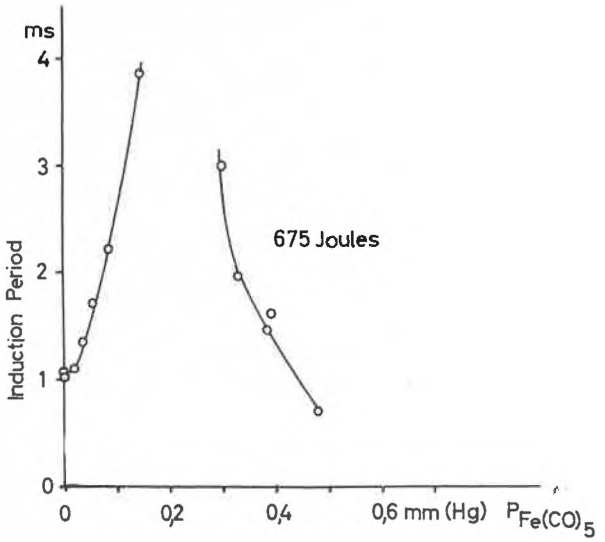

Fig. 2. The induction periods versus pressure of iron pentacarbonyl. – Mixture: 1.5 mm iso-amyl nitrite + 30 mm hydrogen + 22 mm oxygen

tude of the OH emission remains the same the FeO emission becomes larger and larger with increasing amounts of iron pentacarbonyl.[7,8] With higher photolytic energies (1350 Joules ^{x}) the response of the mixture is very moderate and there is also no concentration region of iron pentacarbonyl where no explosion was observed.

Figure 2 shows another set of experiments with a mixture containing 1.5 mm isoamylnitrite + 30 mm hydrogen + 22 mm oxygen. The response to iron pentacarbonyl is again very great. The induction period increases from 1 ms to almost 4 ms. Here the region of no explosion ranges from 0.15 (Hg) to 0.3 mm iron pentacarbonyl. All these results—and many more were obtained—show that iron pentacarbonyl functions as an anti-knock by delaying the autoignition of an explosive mixture similar to TEL. A detailed account of this work will be published elsewhere.

The help of Mr. U. Zysset with all the experiments is acknowledged.

K. Erhard
Monsanto Research S. A., Zürich