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Influence of $Cr(CO)_6$ and $Mo(CO)_6$ on the critical conditions for ignition and the velocities of flame propagation for the chain-branching oxidation of hydrogen and propylene

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It has been found that small additions (~0.1 vol%) of chromium hexacarbonyl and molybdenum hexacarbonyl promote the combustion of a stoichiometric mixture of $H_2 + O_2$, resulting in a lowering of the lower limit of initiated ignition and an increase of the visible velocity of flame propagation; as this takes place, inhibition of propylene oxidation by the additives is observed indicating that hydrogen atoms do not play a noticeable role in chain branching in the initiated oxidation of hydrocarbons at room temperature; this indicates also that the kinetic mechanism of inhibition by carbonyls based on termination by the recombination of hydrogen atoms reported in the literature must be revised. Excited Cr atoms have been observed in a $H_2 + O_2$ flame in the presence of chromium hexacarbonyl.

The production of the effective and widely used fire suppressant CF_3Br (Halon 1301) and other related compounds has been banned due to their contribution to ozone depletion.[1,2] Therefore attention has been directed to the search for alternative compounds. It is well established that some organophosphorus[3] and metallo-organic[1,2,4] compounds (MOC) are very powerful inhibitors of a hydrocarbon flame, being ~100 times more efficient than CF_3Br.[1,2] But they are flammable and highly toxic, so these compounds may find use as fire suppressants only in unoccupied areas.

It has been found[2] that the addition of a MOC [*e.g.* iron pentacarbonyl $Fe(CO)_5$, or ferrocene, $Fe(C_5H_5)_2$] to premixed HC flames at atmospheric pressure at mole fractions of just above a few hundred ppm reduces the burning velocity by 50% and does not further reduce it with an increase in the amount of MOC. The nonlinear dependence of the effectiveness of a MOC based on the amount of iron in the MOC is probably related to the condensation of intermediates involving iron atoms and to the further growth of the particles.[5] The condensation of the particles is accompanied by blackbody radiation,[5] so the main property required for the parent molecule of MOC is that it decomposes at flame temperatures to release atoms of metal. The role of ligands is reduced to providing the solubility of the suppressant in the fuel and also sufficient vapour pressure. Tetraethyl lead provides both these features. Nevertheless, the mechanism of a MOCs action has not been proved experimentally.[1,6,7] In any event, an understanding of the inhibition mechanism of MOCs could provide insight into the behaviour of other highly effective agents and aid in the development of new non-toxic agents.

An inhibition mechanism has been proposed[8,9] for $Fe(CO)_5$. Its decomposition releases iron atoms in the gas phase. Iron reacts with O_2 to form FeO_2, which reacts with an O atom to form FeO. Next FeO, together with $Fe(OH)_2$ and FeOH, enters into the catalytic cycle for the recombination of H atoms in:

$$FeOH + H \rightarrow FeO + H_2,$$
$$FeO + H_2O \rightarrow Fe(OH)_2,$$
$$Fe(OH)_2 + H \rightarrow FeOH + H_2O,$$
$$(\text{net: } H + H \rightarrow H_2).$$

It should be noted that the mechanisms[4] of the suppression of HC oxidation by ferrocene and by MOCs[9] based on tin and manganese are similar to the above. Thus, a conspicuous role of H atoms in HC oxidation is implied. Moreover, one might expect drastic suppression of hydrogen oxidation by MOCs, because H atoms are the main chain carriers in the reaction,[10] and H atoms apparently[4,8,9] mainly recombine *via* an additive.

We emphasize that the experimental evidence on the influence of MOCs on H_2 oxidation is rather scanty. It has been noted[11,12] that MOCs based on Cr, Mn, Sn, U, Mg and Ba at a level of ppm enhance the recombination of H atoms. The suppression of a flame of $CO + H_2 + O_2 + N_2$ at atmospheric pressure by iron pentacarbonyl has been reported;[13] the mechanism based on the results of Rollanson and Plane[14] includes only the termination of O atoms in the sequence of steps:

$Fe + O_2 + M \rightarrow FeO_2 + M$,
$FeO_2 + O \rightarrow FeO + O_2$,
$FeO + O \rightarrow Fe + O_2$,
(net: $O + O \rightarrow O_2$)

though it is known that H atoms play the most important role in CO oxidation.[10] However, according to the experimental measurements,[13] the effectiveness of inhibition is markedly lower than in the case of HC combustion.

It should be noted that the contemporary experiments on the influence of a MOC on the oxidation of an HC refer for the most part to atmospheric pressure with air as oxidant. Measurements of concentration limits and kinetics at lower pressures for the effect of a MOC on the oxidation of an HC by O_2 are missing from the literature.

This work is aimed at the experimental establishment of the peculiarities of the influence of small additives (~10^3 ppm) of $Cr(CO)_6$ and $Mo(CO)_6$ vapour on the oxidation of H_2 and also of an HC such as propylene (C_3H_6). It will allow the mechanisms of suppression based on the termination of H and O atoms to be tested; the use of carbonyls of different metals should reveal the influence of the chemical nature of the metal on the inhibiting effect.

The experiments were carried out under static conditions at 293 K and total pressures of 25–300 Torr. Two quartz cylindrical reactors (4 cm in diameter, lengths 25 cm and 120 cm for reactors I and II) had inlets for gas evacuation, as well as optical windows. Ignition was provided by a spark (0.91 J) at the butt-end of the reactor. The spark was also used to start recording. The reactors were evacuated to 10^{-3} Torr before each experiment. The mixtures of $2H_2 + O_2$ (stoichiometric), $C_3H_6 + O_2$ and $CH_4 + O_2$ were prepared prior to the experiments. Carbonyl vapour was initially allowed to bleed into the evacuated reactor up to the necessary pressure (0.05–0.17 Torr). Then the combustible mixture was admitted up to appropriate total pressure. The mixture containing MOC was kept in the reactor for 10 min for mixing. The lower limit of initiated ignition was determined as the mean of the pressure at which ignition was observed and the pressure at which the ignition did not take place. Chemiluminescence was recorded with FEU-39 photomultipliers (spectral sensitivity 200–600 nm) equipped with an interference filter 306±10 nm (for OH $A^2\Sigma - X^2\Pi$ emission[10]). The visible velocity of flame propagation V_v was recorded using the FEU-39 equipped with three light guides placed 15 cm apart. Note that it was unnecessary to measure normal velocities due to the qualitative character of the investigation. Output signals were recorded by means of a digital oscilloscope and stored in a computer. Emission spectra of initiated ignition were recorded with an OSA-500 optical spectral analyzer (Germany) sensitive over the range 200–900 nm with a resolution of 0.2 nm per channel. The required number of scans (1 scan = 500 channels per 32 ms) was also stored in the computer.

First inhibition of propylene oxidation by $Cr(CO)_6$ and $Mo(CO)_6$ was detected. The dependence of the lower concentration limit for initiated ignition (P_{in}) in reactor I on the concentration of propylene in oxygen, both in the absence and the presence of $Cr(CO)_6$ with saturated vapour pressure[15] of 0.17 Torr, is shown in Figure 1. As is seen, in the presence of $Cr(CO)_6$ the value of P_{in} markedly increases. It is seen also, that the difference between P_{in} in the absence and the presence of $Cr(CO)_6$ is maximal at lower fuel concentrations. Also, it decreases on increasing the ratio $[C_3H_6]/[O_2]$. This means that MOCs are promising inhibitors of lean HC mixtures.

A typical kinetic curve of the chemiluminescence (at 306 nm) during initiated ignition and the dependence of delay periods of initiated ignition (τ) are shown in Figure 2. The delay period τ was considered to be the time interval between the maximal spark emission and maximal emission of OH radicals (Figure 2).

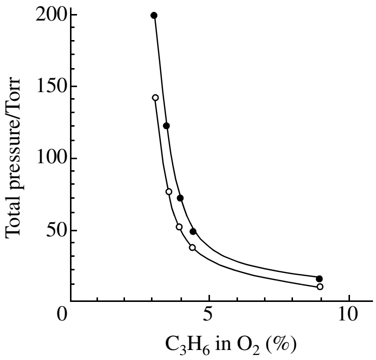

Figure 1 Dependence of the lower limit of initiated ignition (P_{in}) in reactor I on the concentration of propylene in oxygen (empty circles) in the absence and (full circles) in the presence of $Cr(CO)_6$ at a saturated vapour pressure (0.17 Torr).

The dependence of τ on the added $Mo(CO)_6$ is more drastic than for $Cr(CO)_6$, *i.e.,* there is a dependence of the effectiveness of an MO on the metal. Flame velocities were measured in reactor II. It was found that V_v markedly decreases in the presence of MOC, *e.g.*, $V_v = 8.9\pm0.2$ m s^{-1} for $[C_3H_6]/[O_2] = 4.5\%$ at 70 Torr but $V_v = 5.4\pm0.1$ m s^{-1} for these conditions in the presence of 0.1 Torr of $Mo(CO)_6$. It should be noted that V_v at P_{in} accounts for 1.25 ± 0.05 m s^{-1} for $[C_3H_6]/[O_2] = 4.5\%$ and the value is ~7 times lower than for $2H_2 + O_2$ (see below) in agreement with published data.[16]

These results on inhibition also agree with published data: V_v can decrease by ~50%. Therefore, molecules of MOC may be assumed to decompose in the flame front, forming metal atoms, which react rapidly with oxygen. Condensation of molecules (these are most likely to be oxides) produces nanoparticles, which cause inhibition by enhancing the rate of chain termination. In this connection it should be noted that coatings of a transition metal oxide inside a reactor are very effective at terminating chains by providing sufficient area for radicals to diffuse to the walls.[17]

We expected to detect similar features when investigating the influence of MOC on the oxidation of hydrogen. However, the effect of the additives was the opposite of that for propylene oxidation. Thus, P_{in} of a stoichiometric mixture of hydrogen in oxygen ($2H_2 + O_2$) in the presence of 0.1 Torr $Mo(CO)_6$ decreased from 35 Torr (without an additive) to 31 Torr under our condi-

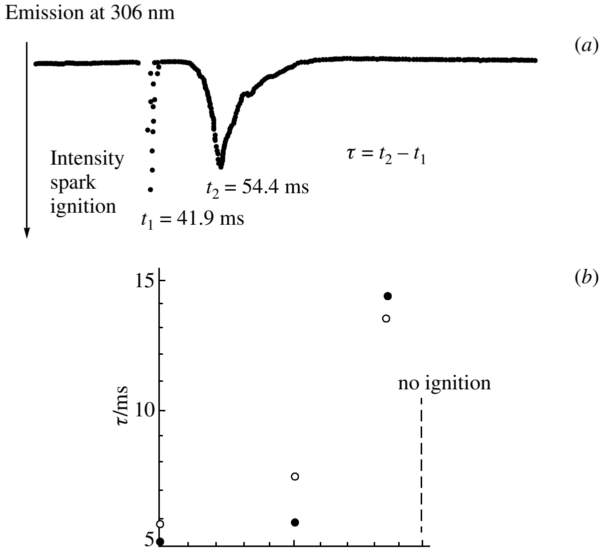

Figure 2 (*a*) Typical kinetic curve of the chemiluminescence (306 nm) of initiated ignition [total pressure, 45 Torr; 0.13 Torr $Cr(CO)_6$; 4.5% C_3H_6 in O_2]. (*b*) Dependence of delay periods of initiated ignition (τ) on the partial pressure of (empty circles) $Cr(CO)_6$ and (full circles) $Mo(CO)_6$ [4.5% C_3H_6 in O_2; total pressure, 40 Torr].

tions; in the presence of 0.1 Torr $Cr(CO)_6$ decreased to 28 Torr. This also clearly demonstrates that the effectiveness of an MO depends on the nature of metal. The values of τ also decreased, *e.g.*, from 1.35±0.1 ms at 36 Torr (without an additive) to 0.8±0.1 ms at 34 Torr in the presence of 0.1 Torr $Mo(CO)_6$. Also, V_v markedly respectively increased from 8.2±0.2 m s^{-1} at 43 Torr $2H_2 + O_2$ to 55±3 m s^{-1} in the presence of 0.12 Torr $Mo(CO)_6$ and to 65±3 m s^{-1} in the presence of 0.12 Torr $Co(CO)_6$.

For both systems investigated initiated ignition in the presence of MOC was accompanied by intense radiation with a continuous spectrum – blackbody radiation over the range 400–900 nm in agreement with the literature.[8] The spectrum does not have a banded structure and therefore it possibly originates from the formation of solids, *e.g.*, of nanoparticles of metallic oxides. However, strong resonance chromium bands (425.4, 427.4 and 429 nm) have been observed[18] in the spectrum of initiated ignition of stoichiometric $H_2 + O_2$ mixture in the presence of $Cr(CO)_6$. In fact, these bands are ~10 times less intense in the spectrum of the ignition of stoichiometric $CH_4 + O_2$ mixture (Figure 3). The occurrence of metal atoms in a $H_2 + O_2$ flame in the presence of MOC is immediately evident from [Figure 3, curve (*1*)]. In this case, the concentration of metal atoms in a HC flame in the presence of MOC is markedly lower. Note that the excitation of Cr atoms has a chemical nature, because the temperature-rise in stoichiometric $H_2 + O_2$ flames under our conditions is ~2000K.[19] The chemical mechanism of the excitation needs further investigation.

Detection of the promoting action of $Co(CO)_6$ and $Mo(CO)_6$ on hydrogen oxidation, in which hydrogen atoms are the main chain carriers, points to the fact that the mechanism of inhibition based[8,9] on the recombination of H atoms should be revised.

Furthermore, the phenomenon revealed is immediate evidence that hydrogen atoms do not in essence take part in chain-branching in hydrocarbon oxidation under conditions of initiated ignition at room temperature, contrary to certain contemporary notions.[20] In our opinion, a dimensional effect, implying that the chemical properties of nanoparticles markedly differ from those of the bulk material,[21] plays a governing role in the observed promotion of $H_2 + O_2$, but inhibition of propylene oxidation with a MOC. Whereas the rate of termination of hydrogen atoms on the bulk metal oxide surface is high,[17] nanoparticles containing metal atoms react in another way with chain carriers of the $H_2 + O_2$ reaction. This way is somewhat similar to the promoting action of bulk platinum on this reaction.[22] In addition, hydrogen atoms may prevent a metal from oxidising, due to their reducing ability. Therefore non-oxidised metal particles in the $H_2 + O_2$ reaction exhibit a promoting action; on the other hand, a metal oxide exhibits inhibiting action in the case of oxidation of hydrocarbons, where the role of hydrogen atoms is insignificant, as mentioned above.

Note that the promoting action of the bulk surface on both ignition and combustion under almost isothermal conditions has been described previously.[23] It was also shown[23] that the phenomenon is caused by heterogeneous development of chains. The experimental observations in this work demonstrate the ability of a surface of nanoparticles formed in the thermal decomposition of a MOC to promote ignition and combustion as well.

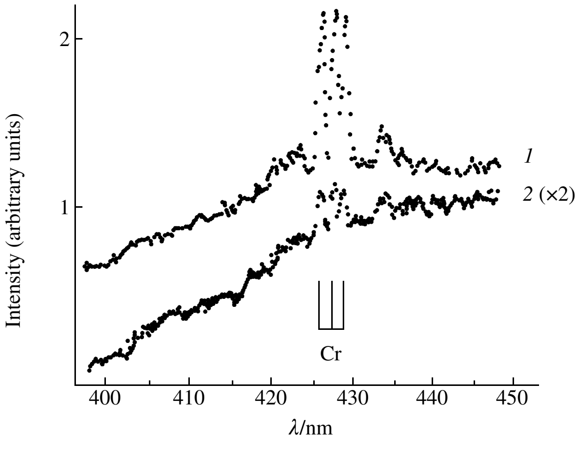

Figure 3 Emission spectra of initiated ignition over the range 400–450 nm recorded using reactor I: (*1*) stoichiometric mixture of $H_2 + O_2$ in the presence of 0.17 Torr $Cr(CO)_6$, total pressure, 200 Torr; (*2*) 29% $CH_4 + O_2$ in the presence of 0.17 Torr $Cr(CO)_6$, total pressure, 200 Torr.

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References

1 J. W. Hastie, *Journal of Research of the National Institute of Standards and Technology*, July–August, 2001, 201.

2 G. T. Linteris, M. D. Rumminger, V. Babushok and W. Tsang, *Proc. 28th International Symposium on Combustion*, Edinburgh, Scotland, 2000, pp. 1–22.

3 T. M. Jayaweera, C. F. Melius, W. J. Pitz, C. K. Westbrook, O. P. Korobeinichev, V. M. Shvartsberg, A. G. Shmakov, I. V. Rybitskaya and H. J. Curran, *Proc. Joint Meeting of the Combustion Institute*, Oakland, CA, 2001, pp. 33–56.

4 M. D. Rumminger, D. Reinelt, V. Babushok and G. T. Linteris, *Halon Options Technical Working Conference*, Albuquerque, NM, 1998, pp. 1–12.

5 G. T. Linteris and D. Reinelt, *Proc. INTERFLAM'96, Seventh International Fire Science and Engineering Conference*, Cambridge, 1996, p. 477.

6 A. S. Sokolik, *Samovosplamenenie, plamya i detonatsiya v gazakh* (*Ignition, Flame and Detonation in Gases*), USSR Academy of Sciences, Moscow, 1960 (in Russian).

7 R. Friedman and J. B. Levy, *Combustion and Flame*, 1963, **7**, 195.

8 D. Reinelt, V. Babushok and G. T. Linteris, *Eastern States Section Meeting of The Combustion Institute*, Hilton Head, SC, 1996.

9 G. T. Linteris, V. D. Knyasev and V. Babushok, *Combustion and Flame*, 2002, **129**, 221.

10 N. N. Semenov, *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (*On Some Problems of Chemical Kinetics and Reactivity*), USSR Academy of Sciences, Moscow, 1958 (in Russian).

11 E. M. Bulewicz and P. J. Padley, *Proc. Combust. Inst.*, 1971, **13**, 73.

12 G. Linteris, *Limits to Effectiveness of Metal-Containing Fire Suppressants, Final Technical Report to SERDP*, National Institute of Standards and Technology, Gaithersburg, MD, 2004.

13 M. D. Rumminger and G. T. Linteris, *Combustion and Flame*, 2000, **120**, 451.

14 R. J. Rollason and J. M. C. Plane, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2335.

15 I. Barin, *Thermodynamical Data of Pure Substances*, VCH Verlag, Berlin, 1989, Part I–II.

16 *Pozharo i vzryvobezopasnost veshchestv i materialov i sredstva pozharotusheniya* (*Fire and Explosion Safety of Substances and Materials and the Means of Fire Control*), Handbook, eds. A. Ya. Korol'chenko and A. N. Baratov, Khimiya, Moscow, 1990, vol. 1, p. 360 (in Russian).

17 V. V. Azatyan, *Usp. Khim.*, 1985, **54**, 33 (*Russ. Chem. Rev.*, 1985, **54**, 21).

18 R. Pierse and A. Gaydon, *The Identification of Molecular Spectra*, Academic Press, New York, London, 1941.

19 B. Lewis and G. Von Elbe, *Combustion, Explosions and Flame in Gases*, Academic Press, New York, London, 1987.

20 W. L. Grosshandler, *Proc. Symposium on Thermal Science and Engineering in Honor of Chancellor Chang-Lin Tien*, Berkeley CA, 1995, p. 275.

21 C. F. Landes, M. Braun and M. A. El-Sayed, *J. Phys. Chem. B*, 2001, **105**, 10554.

22 V. V. Azatyan, Yu. I. Pyatnitskii, N. A. Boldyreva and N. A. Klimova, *Khim. Fiz.*, 1988, **7**, 235 (in Russian).

23 V. V. Azatyan, *Zh. Fiz. Khim.*, 1998, **72**, 199 (*Russ. J. Phys. Chem.*, 1998, **72**, 319).

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