Detection of hydrogen atoms and their distribution in the front of stabilized cool hydrocarbon flames.

Z.A. Mansurov, B.A. Urmashev, O.A. Auelbekov
Al-Farabi Kazakh National University
Department of Chemical Physics, Almaty, Kazakhstan
e-mail: mansurov@kazsu.kz

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Introduction
In recent years the interest to hydrocarbon cool flames increased from the point of view of their practical application [1,2]. In [2] cool flame oxidation is used as generator of free radicals are peroxide radicals maximum of which coincides with the appearance of cool flames [3]. A characteristic property of cool flame is light-blue luminescence of excited formaldehyde the decomposition of which results in the formation of hydrogen atoms which is more active that peroxide radicals [4].

Detection of hydrogen atoms by EPR method and estimation of their concentration in a low temperature zone are difficult, firstly, due to their low concentration and, secondly, high reactivity that, in combination with oxidation incompleteness in this zone, results in interaction of radicals in sampler canal with molecular hydrogen, initial fuel and radical recombination reactions. Hydrogen and oxygen atoms are stated to be detected only in that part of flame where fuel conversion is already completed [4,5].

To detect hydrogen atoms in stabilized cool flames it is apparently expedient to use the known method of trapping the radical [6,7] with conversion of hydrogen atom into a final product.

In the present work carbon tetrachloride is used as an additive which carries out trapping of H-atoms according to the reaction with the formation of HCl

\[ \text{H}^+\text{CCl}_4 \rightarrow \text{HCl} + \text{CCl}_3. \]

The method of amperometric titration [8] was used to determine the concentration of the latter.

The aim of the present work is detection of hydrogen atoms in the front of stationary cool flames and determination of its reactivity.

Experimental
To investigate the structure of the front of stabilized cool flames of butane with the aim to obtain a flat, one-dimensional flame front, a two-section reactor the sections of which is divided by a perforated plate made of Pyrex (fig. 1) was used. The perforated plate is a disk with 50 holes on all the area, the summary area of holes is 50 mm². The reactor is a Pyrex cylinder with the inside diameter of 62 mm, the length of the first section is 30 mm, and that of the second one is 100 mm, it is established in a vertical position and the combustible mixture is supplied from below into the first section. The reactor is placed into a thermostat where thermostatting is reached by forced mixing of hot air flows.

![Fig. 1 Heated reactor of a flat flame.](image)

1 - Thermostat, 2 - The first section, 3 - The second section, 4 - Perforated plate, 5 - Thermocouples, 6 - Heating coils, 7 - Fan.
To detect H atoms, the technique combining the method of trapping radicals [9] with the supply of an additive near the sampling point was used.

Carbon tetrachloride was used as additive to trap H atoms with the following determination of chlorine ion concentration by amperometric titration. Figure 2 presents the scheme of the unit consisting of a vessel with CCl₄ (1), a furnace for heating CCl₄ (2), a quartz probe for sampling from the flame (3), a capillary to supply CCl₄ (4) and a trap to freeze out a sample (5). Diameters of the hole and probe and the capillary are the same and equal to 70 mcm. Freezing was carried out with liquid nitrogen. On the basis of optimization of the experiment conditions, CCl₄ was supplied at the temperature of the furnace 520 K and constant mixing; the sampling time was 1 hour, the sample volume was 0.2 – 0.3 ml.

![Fig. 2. The unit scheme.](image)

1 – vessel with CCl₄, 2 – furnace for heating CCl₄, 3 – quartz probe for sampling from the flame, 4 – capillary for supplying CCl₄, 5 – trap for freezing out the sample, 6 reactor.

In the obtained sample after freezing, using the method of amperometric titration, the concentration of chlorine ions was determined which was equal to the number of H-atoms.

\[ C_{Cl} = \left( \frac{C_{Cl}}{E_{Cl}} A (H) 100 \right) \times 6.023 \times 10^{23} \]

Then concentration of hydrogen atoms per 1 sec. in the sampling point was determined by the formula:

\[ [H] = \frac{C_{Cl}}{Q \cdot t}, \] where \([H]\) – concentration of H-atoms, particles/cm³, \(Q\) – probe capacity, cm³/s, \(t\) – sampling time, s.

**Results and discussion**

Experiments on detection of hydrogen atoms were carried out with cool stabilized butane flames. The experiments were carried out at atmospheric pressure with the ratio C₄H₁₀:O₂=1:2, T₁=443K, T₂=733K. The diameter of the inlet hole of the quartz probe was \(d = 70\) mcm.

Figure 3 shows profiles of hydrogen atoms and temperature in the front of stabilized cool butane flame. As it is seen, maximum concentration of hydrogen atoms is 1.6\( \times 10^{11}\) cm⁻³ which somewhat advances temperature maximum by time. It should be noted that minimum concentration of hydrogen atoms in the butane flame is equal to 3.0\( \times 10^{10}\) cm⁻³ at temperature 593 K, i.e. 5 times less than maximum concentration. The obtained result is similar to the data on peroxide radical profile concentrations when probing the cool flame of diethyl ether [10] described in the previous section as well as by data obtained by Mantaschyan with his co-workers [11] in the investigation of cool flame oxidation of propane.

![Fig. 3 Temperature and hydrogen atom concentration profiles T₁ = 443 K, T₂=730 K, C₄H₁₀ : O₂ = 1 : 2.](image)
The obtained by us for the first time profiles of H-atom concentration in cool hydrocarbon flames are evidence of their important role in the pre-flame zone of normal flame flouts which may be considered as incomplete cool flame. Let us consider possible canals of hydrogen atom formation. G.I. Ksandopulo [4], analyzing the results of probing hydrocarbon flame front, came to the conclusion that on the curves of hydrogen atom concentration profile in the perfume front part there is observed an area indicating the presence in this zone of its own source of hydrogen atoms. As such, the decomposition reaction of excited formaldehyde is taken.

\[
\text{CH}_2\text{O} + M \rightarrow \text{CHO} + H + M
\]

The principle possibility of such branching is possible because of the luminescence of cool flame was caused by excited formaldehyde [12].

One may carry out analysis of oxidation reactions which may be considered as source of hydrogen atoms in the temperature regime of cool flames. From reference data on hydrocarbon oxidation rate constants the following reactions may be considered as reactions leading to the formation of hydrogen atoms in the regime of cool flames. From reference data on hydrocarbon oxidation rate constants the following reactions may be considered as reactions leading to the formation of hydrogen atoms [13]:

\[
\begin{align*}
\text{CH}_2 + M & \rightarrow \text{"CHO} + H^* + M \quad (M = \text{Ar}) \\
\text{CH}_3\text{O} + \text{CH}_3\text{OH} + M & \rightarrow \text{CH}_2\text{O} + H^* + M \\
\text{CH}_3\text{O} + \text{CH}_2\text{OH} & \rightarrow \text{"CHO} + H^* \\
\text{"CHO} + M & \rightarrow \text{CO} + H^* + M \\
\text{CH}_2\text{H}_5 + M & \rightarrow \text{C}_2\text{H}_4 + \text{ H}^* + M \\
\text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + H^*
\end{align*}
\]

For convenient choosing of the most preferable reactions in the regime of cool flames, constant data were taken for the temperature range of cool flame 400-770K. The comparison of data allows to conclude that reactions with activation energy more than 105 kJ/mole are less probable at that temperatures. On the bases of rate constant analyses it may be supposed that hydrogen atom formation in the regime of cool flames is possible as a result of the reactions:

\[
\begin{align*}
\text{CH}_2\text{O} + M & \rightarrow \text{"CHO} + H^* + M \\
\text{CH}_3\text{O} + M & \rightarrow \text{CH}_2\text{O} + H^* + M
\end{align*}
\]

alongside with which parallel and reactions of HCO formation are possible followed by a quick decomposition and generation of H atoms

\[
\begin{align*}
\text{CH}_2\text{CHO} & \rightarrow \text{CH}_3 + \text{ CHO} \\
\text{CH}_2\text{O} + \text{CH}_3 & \rightarrow \text{ CHO} + \text{ CH}_4 \\
\text{CH}_2 + H^* & \rightarrow \text{ CHO} + \text{ H}_2 \\
\text{ CH}_2 + \text{ O}_2 & \rightarrow \text{CH}_2\text{O} + \text{ H}^* + \text{ O}^* \\
\text{HCO} + M & \rightarrow \text{H} + \text{ CO} + M
\end{align*}
\]

Thus, the source of hydrogen atoms is formaldehyde, radicals CH3, HCO.

Let us try now to estimate the role of hydrogen atoms in cool flame oxidation of hydrocarbons. For comparison we should calculate interaction rate constants of carbon with the mentioned radicals at T=600 K corresponding to our experimental data.

\[
\begin{align*}
\text{RH} + \text{ H} & \rightarrow \text{ R}^* + \text{ Y}_2 \\
\text{RH} + \text{ RO} & \rightarrow \text{ R}^* + \text{ ROOH}
\end{align*}
\]

Kinetic data of the mentioned reactions are taken from the review by Lignola and Reverchon [14] for cool flame regimes (500-800K).

Let us substitute now rate constant values and concentration values of hydrogen atoms and RO2. The value of RO2 concentration is taken from the work on probing the cool flame of diethyl ether [9] in the point where temperature is equal to 600 K and following expression is obtained:

\[
W_1 = \frac{K_1[H]}{K_2[RO_2]} = \frac{3.1 \cdot 10^{14} e^{-\frac{35600}{R \cdot 600}} \cdot 1.4 \cdot 10^{11}}{3.2 \cdot 10^{11} e^{-\frac{68900}{R \cdot 600}} \cdot 2.2 \cdot 10^{14}} = 4.8 \cdot 10^2
\]

Thus, it is seen that despite the fact that hydrogen atom concentration is 100 times less than the concentration of peroxy radicals, fuel conversion reactions with atom participation proceed 480 times quicker. On the basis of the given estimation of rate of interaction of hydrogen atoms and peroxy radical with hydrocarbons one may make the conclusion about a significant role of hydrogen atoms in cool flame oxidation reactions. It may be supposed that the important role of hydrogen atoms is in a quick conversion of fuel molecules into alkyl radicals.
Let us briefly give the main results on the study of distribution of hydrogen atoms in the front of stabilized hydrocarbon cool flames:
- maximum hydrogen atom concentrations are observed in the luminescent zone of cool flame front;
- for the first time in cool flames of butane, hydrogen atoms were detected and their concentration profile was obtained, and a significant role of hydrogen atoms in the mechanism of cool flame oxidation was stated;
- combined consideration of profiles of temperature and concentrations of hydrogen atoms and peroxide radicals allows to suppose that hydrogen atoms from the luminescent zone diffuse to the side of a fresh mixture. Due to their extreme activity and more and more increasing concentration of initial substances to the coordinate origin, the region of penetration of hydrogen atoms into a fresh mixture is greatly limited. At the same time the extent of the zone of peroxide radical effect to the side of fresh mixture is considerably greater which can be accounted for their low activity and concentration.

**Literature**