Modeling of the phenomenon of the birth of weak shock waves in the oxidation of hydrogen and hydrocarbons at the presence of surface active centers (water + negative ion of chlorine).

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Annotation:

In this work, to explain our experimental data on the registration of pulsations of light emission of the reaction, at low temperature ($T \approx 600K$) oxidation of organic compounds and hydrogen, the possibilities of computer modeling are used. By the help of computer mathematical programs ChemBio 12,00, Gaussian, and MATCAD, the effect of adsorbed on the surface of reactors complexes of negative halogen ion and water molecule ($H_2O \cdot Cl^-$), on the process of chain oxidation, due to the formation of molecules ozone a product of ionic processes.

The sharp heat release in a local place of the reactor due to the decay of ozone, can leads to the birth of both concentration traveling waves and weak shock waves in the reactors.

A similar model is also being investigated in the case of hydrogen oxidation.

Key words: chain oxidation, ionic complexes, weak shock waves.

Introduction

Chain processes with a multichannel character are inherent in a difficult way to achieve equilibrium, due to the interconnection of elementary acts, sensitivity to relaxation processes and energy redistribution also to external factors. These phenomena greatly affect the productivity and safety of chemical gas phase reactors, when obtaining the target product, as well as the establishment of dynamic modes on which these phenomena depend.

A fundamental role in this can be played by the processes caused by the presence of complexes of negative ions with water at the surface of the reactor, causing a chain of ion-molecular reactions (IMR), preceding several orders of magnitude faster than reactions with the participation of free radicals.In the volume, as is known [1], ionic processes lead mainly to the formation of ionic clusters, and in the near-surface layer, ionic complexes with water fixed on the surface layer can, bring the initiation of charge exchange reactions and ion-molecular reactions, as the results of computer simulation show, accelerating the formation of intermediate easily decaying products heating the reaction mixture in a local place, as a result of which weak shock waves may be generated in the reactor [2].

In this work, we consider the effect of surface active centers (by the example of adsorbed on the surface complexes of water molecules with a negative halogen ion) as a source of formation of weak shock waves.

As is known, processes occur immediately behind the shock front in a narrow layer that lead to an intense increase in temperature and then the transfer of thermal energy into internal energy [3].

Theoretical part: The basis of the model is the processes that lead to the transformation of the intermediate product of the hydrogen and organic compounds reactions of H_2O_2 into ozone O_3 molecules, the self-decomposition or reaction of which leads to the release of a large amount of heat in the local place of the reactor (places of concentration of water + negative halogen ion complexes) due to the chain of processes [2]:

$$\begin{aligned} &H_2O_2 + H_2O{\cdot}Cl^- \rightarrow H_2O{\cdot}O^- + H_2O{\cdot}Cl \\ &H_2O{\cdot}O^- + O_2 \rightarrow H_2O + O_3^- \qquad (1) \\ &O_3^- + H_2O{\cdot}Cl \rightarrow O_3 + H_2O{\cdot}Cl \end{aligned}$$

In next picture Figure: 2, schematically presented the possibility of formation of resonant conditions after impact of H_2O_2 molecules on complex $H_2O \cdot Cl^-$ located nearly surface.

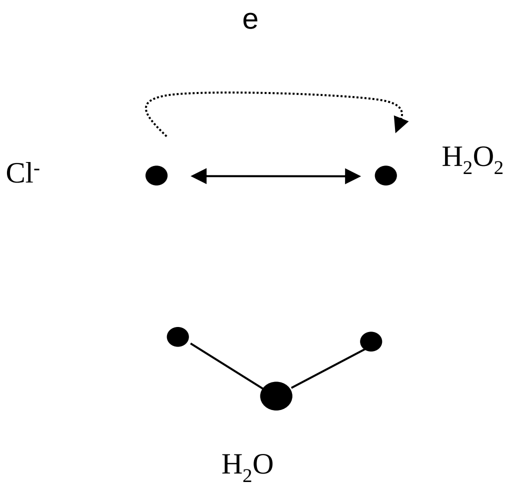

Figure: 2. Schematic representation of the appearance of resonant conditions for recharge.

In Fig. 3, is presented the possibility of an decomposition of the formed complex $\{O_3 \cdot H_2O \cdot Cl^-\}$ after formation, calculated in turn using the MM2 Minimize and MM2 Dinamics programs within the ChemBio 12.0 software package.

Fig. 3. The picture of the self-decomposition of the complex $\{O_3 \cdot H_2O \cdot Cl^-\}$ after formation, due to heating, calculated using the MM2 Minimize and MM2 Dynamics programs within the ChemBio 12.0 software package.

As are shown in the work [2] the existence of the first act is justified by the closeness of the electron affinity of the chlorine atom and hydrogen peroxide molecules Ae (H_2O_2) = 3.02 eV [4] and Ae (Cl) = 3.62 eV [5] and absorption of the energy released during scattering (capture of H_2O_2 by the $H_2O\cdot Cl^-$ complex) an extra electron of a negative chlorine ion.
The estimation of the interaction energy (E) of a peroxide molecule with a negative chlorine ion, due to collision, can be carried out in the approximation of a point dipole and a point charge [1]:

At a distance of 3.2 Ǻ approximately 0.613 eV energy is released, which, when both particles are equally distant from the water molecule (see Fig. 2), the electron transition process will become resonant.
This leads to the possibility of a resonant electron transition from Cl^- to H_2O_2. To estimate the cross section of the electron transfer act leading to the appearance of a complex ion (H_2O) O^-, one can use the well-known formula obtained for calculating the rate constant of ionic processes by the torsion mechanism [6]:

After the capture of an electron, the formed negative peroxide ion changes its structure and transforms into a complex consisting of a water molecule and an oxygen anion [1] $(H_2O_2)^- \rightarrow (H_2O)O^-$.

In this approximation, according to formula (3), for the rate constant of the recharge process $(H_2O)Cl^- + H_2O_2 \rightarrow (H_2O)Cl + (H_2O)O^-$, the value $k_1 \approx 3 \cdot 10^{-10}$ cm^3 / molecule s.

The second act is well known from the literature [1] with the rate constant $k_2 \approx 10^{-11}$ cm^3 / molecule, s.

The third act is strongly exothermic and the rate constant of this transformation calculated by formula (3) is $k_3 \approx 10^{-10}$ cm^3 / molecule s.

Taking into accounts, that in temperatures $T \geq 600K$ the channel of self-decay of ozone $O_3 \rightarrow O + O_2$ is more effective $\tau << 0.02$seconds, the basic role will be play the self-decay [7].

The problem is similar to the point explosion phenomenon. But it is better to consider this task in terms of ideal gas as was first done by R. Becker [8] in the limit of.Hugionio theory,

In the limit of these theory is shown that in the case of ideal gas conditions the shook wave front may be born at the distance $10^{-4} \div 10^{-6}$ cm [8, 9].

Based on the equation of state of an ideal gas, in dimensionless variables, the adiabates of Hugionio are written as [9]:

$$M(V,T) = T/V + V - 1 \qquad (4)$$
$$L(V,T) = T/\gamma\text{-}1 - 1/2(V-1)^2 - \beta$$

where - V - flow volume, T – temperature, $\gamma = c_p/c_v$ - heat capacity ratio,

β - flow constant, which determines the relative position of the Hugionio adiabats.

It should be noted that at V=1it can be determine the value of $\beta = \varepsilon = T/\gamma\text{-}1$.

If the parabolas M (V, T) = 0 and L (V, T) = 0 in the phase space (V, T) intersect at two points, then a shock wave can be generated in the system.

As the calculation results show within the limits of the Gugionio theory [9] (see Fig. 3), there is an intersection of the adiabates of Hugionio.

The calculation of this problem by the help of MATCAD program is presented.

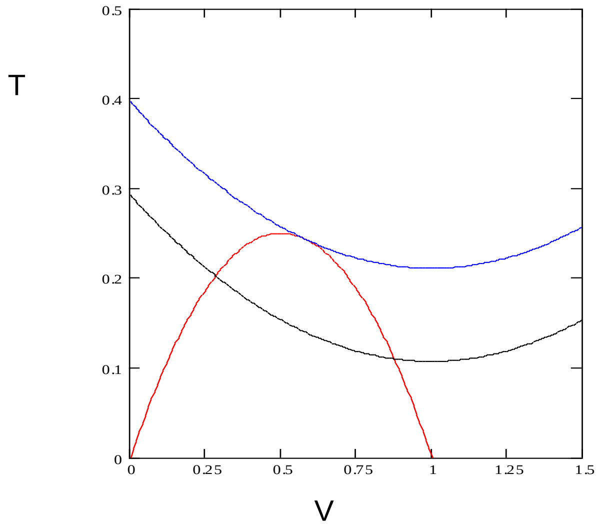

Figure: 4. Mutually location of the adiabates of Hugionio on the phase plane (V, T) calculated by the formula (4) is presented at oxidation of propane, T = 600K .

The theory in the case of weak shock waves presents the possibility of determining the velocity of a thin layer (d = $10^{-4} \div 10^{-6}$ sm) of a shock wave front.

$D = c(1+\varepsilon)$.

where c –velocity of sound; ε - energy of gas; D - velocity of shook wave.

In above mentioned case $D = 330(1+0.29) \approx 425$ m/s.

The calculation using the MATHCAD program of the system of equation in the case of hydrogen oxidation is given below:

Oxidation of Hydrogen with Oxygen

For a estimation of the value of energy release within limit of one millimeter closely to surface layer we will take:

$H_2O_2 \approx 3 \cdot 10^{13}$ molecule / cm^3 and, accordingly, the value for the energy is received $\varepsilon = 0.208J$

In this case is considered the system of $H_2 + O_2$ as y ideal two atomic gases and consequently the parameter $\gamma = 1.4$, $\beta_0 = 0.52083$, $\beta = 0.208$.

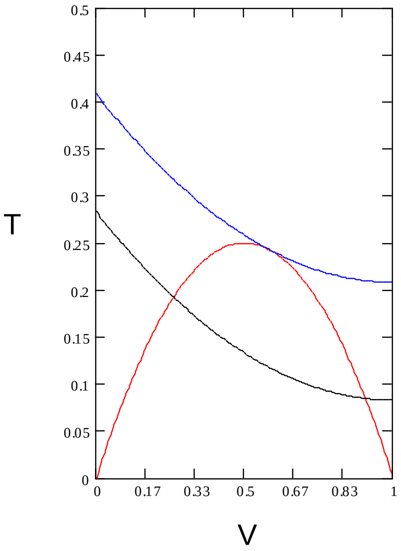

Figure: 6. Mutually location of the adiabates of Hugionio on the phase plane (V, T) calculated by the formula (4) in the case of hydrogen oxidation is presented.

For the velocity of shook wave is received $D = 330(1 + 0.208) \approx 400$ m/s.

Experimental results

During the initiation of the reaction, when in a closed reactor with stirring in a mixture of C_3H_8 + air, at a temperature of T = 600K, no radiation is observed for about three minutes, after which the reaction medium begins to in a pulsed mode

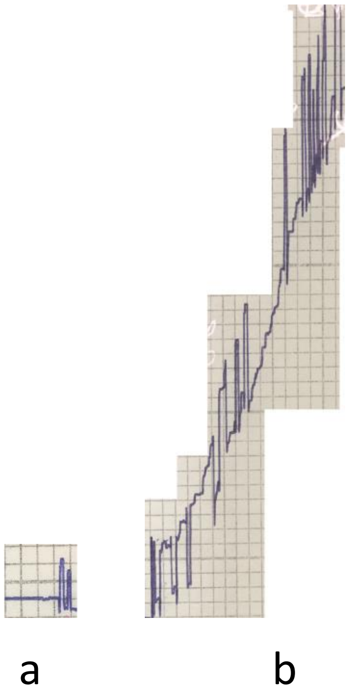

Figure: 7. (a) Initiation of the propane oxidation process with a closed reactor for 3 minutes at a temperature of T= 600 K, (b) after initiation, the reactor is brought into a flow condition with a continuous increase in the mixture pressure (first, the air inlet opens, and then propane

Discussion

The results obtained allow us to conclude that complex ions fixed on the surface of the reactor can become sources of emission of a large amount of energy in a local place of the reactor near the surface.

Released energy in a local place will generate a strong flux to the center of the reactor, which, under the number of such complexes per unit surface $\sim 10^{14}$ square centimeter, and at concentration of hydrogen peroxide $\sim 4 \cdot 10^{13}$ molecules /cm^3, can arise as shock wave (weak shock waves).

The birth of weak shock waves is observed at the initiation of the process, when there is no equilibrium or at a strong acceleration of the process, when the equilibrium is also disturbed by a continuous increase in pressure in the reactor due to the filling of fuel. The flow to the center of the reactor is enhanced due to the intensification of the reaction leading to an increase in the concentration of hydrogen peroxide. Because of this, a large amount of ozone is formatted, a highly heating and accelerating flow, which turns into a supersonic shock wave with a front thickness of $10^{-4} \div 10^{-6}$ cm.

In this case, the representationc developed for the case of a point explosion are applicable, when the appearance of a large amount of energy at a certain point in space leads to the appearance of a shock front in the medium. However, this theory is more applicable to the generation of strong shock waves.

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