ON THE NEGATIVE TEMPERATURE COEFFICIENT IN THE OXIDATION OF HYDROCARBONS

![Fig. 1](figure)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE NEGATIVE TEMPERATURE COEFFICIENT IN THE OXIDATION OF HYDROCARBONS

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A characteristic feature of the oxidation of hydrocarbons is the presence, in a certain temperature region, of the so-called negative temperature coefficient ($^{1-11}$). Figure 1 presents a curve, typical for the oxidation of hydrocarbons, of the dependence of the reaction rate on temperature.

Fig. 1

The temperature interval between the two extrema is called the region of the "negative temperature coefficient." The maximum usually lies in the range 350—400°, and the minimum 450—500°. Depending on the nature of the hydrocarbon, the pressure, the composition of the mixture, the state of the surface, and other factors, the boundaries of the region may shift with temperature.

The existence of the region of the negative temperature coefficient has a strong influence on the kinetics of slow oxidation, the position of limits, and the character of self-ignition of hydrocarbons. However, up to the present time this phenomenon has not received a rational explanation. Detailed consideration shows that the existing theories ($^{6,12-14}$) in fact did not explain the phenomenon of the negative temperature coefficient.

In the present work, on the basis of N. N. Semenov' s theory of degenerate branching (^{15}), the phenomenon of the negative temperature coefficient is considered as the result of competition between elementary processes participating in a complex chain reaction.

It is generally recognized that at low temperatures the oxidation reaction of hydrocarbons proceeds through peroxide radicals formed by the reaction

$$\dot{\mathrm{R}} + \mathrm{O}_2 \rightarrow \mathrm{RO\dot{O}}. \tag{1}$$

This process is characterized by a small steric factor ($10^{-3} \div 10^{-4}$) and a low activation energy ($2 \div 4$ kcal/mole). The elementary process of degenerate branching, in accordance with B. Lewis and G. Elbe (^{13}) and V. V. Voevodskii and V. I. Vedeneev (^{16}), may be represented as the result of the interaction of a peroxide radical with a stable intermediate product, for example with an aldehyde,

$$\mathrm{RO\dot{O}} + \mathrm{R'CHO} \rightarrow \mathrm{\dot{R}O} + \mathrm{\dot{O}H} + \mathrm{R'\dot{C}O}. \tag{2}$$

As a result of such a reaction, three new active centers are formed from one radical. The endothermicity of this process is about 10 kilocalories per mole (^{16}).

The peroxide radical $\mathrm{RO\dot{O}}$, along with reaction (2), which leads to branching, may also enter into a propagation reaction (^{17})

$$\mathrm{RO\dot{O}} \rightarrow \mathrm{R'CHO} + \mathrm{R''\dot{O}}. \tag{3}$$

Reaction (3) proceeds with prior isomerization of the peroxy radical and therefore has a high activation energy (20 kcal/mole)^(18).

Competition between reactions (2) and (3) will lead to the appearance of a maximum on the curve in Fig. 1. Indeed, at low temperatures the peroxy radical must react by the bimolecular reaction (2), which proceeds with a lower activation energy (10–12 kcal/mole). As the temperature rises, the rate of this process increases, which leads to an increase in the rate of the hydrocarbon oxidation reaction. Beginning at a certain temperature (corresponding to the maximum rate on the curve in Fig. 1), the monomolecular propagation reaction (3), proceeding with a higher activation energy, begins to predominate over the branching reaction (2), which leads to a decrease in the rate of the oxidation reaction. At these temperatures the rate of the oxidation reaction is determined not by process (3), as was the case at lower temperatures, but by the reaction of formation of the peroxy radical (1), since the latter is characterized by a small steric factor, although it has a low activation energy. Since the limiting stage of the process becomes reaction (1), the destruction of active centers is determined mainly by the destruction of radicals R. Thus, as the temperature increases, on the one hand, owing to competition between the two parallel reactions of the peroxy radical (2) and (3), the probability of branching decreases; on the other hand, the stationary concentration of ROO radicals decreases, since reaction (1) becomes the limiting process. As a result, the rate of the hydrocarbon oxidation reaction falls sharply as the temperature rises.

The decrease in the rate of the oxidation reaction will occur up to a certain temperature (corresponding to the minimum on the curve in Fig. 1). With further increase in temperature, the reaction rate will again begin to rise, since degenerate branching of another type^(19) will come into effect,

$$\mathrm{RCHO} + \mathrm{O_2} \rightarrow \dot{\mathrm{R}}\mathrm{CO} + \dot{\mathrm{H}}\mathrm{O_2}. \tag{4}$$

This type of degenerate branching was proposed by N. N. Semenov^(15) and was used by us in considering the mechanism of methane oxidation^(17). Elementary process (4) is strongly endothermic, and therefore it should be taken into account only at comparatively high temperatures (after the rate minimum on the curve in Fig. 1).

In this way one may qualitatively represent the appearance of a region of negative temperature coefficient in the oxidation of hydrocarbons.

Starting from such a simplified scheme of hydrocarbon oxidation and taking into account that the rate of branching is less than the rate of chain propagation, for the reaction rate we obtain the expression:

$$W = \frac{W_0 a_3}{g_1 + \dfrac{g_2}{a_1} a_3 - 2a_2}, \tag{5}$$

where W is the rate of the hydrocarbon oxidation reaction, W_0 is the rate of initiation of active centers, g_1 is the constant for the destruction of ROO radicals, g_2 is the constant for the destruction of $\dot{\mathrm{R}}$ radicals, $a_1 = K_1[\mathrm{O_2}]$; $a_2 = K_2[\mathrm{X}]$; $a_3 = K_3$; [X] is the concentration of the intermediate product responsible for degenerate branching (aldehyde).

It follows from equation (5) that, under the given conditions, the reaction rate is determined by the concentration of aldehyde [X], the maximum of which corresponds to the maximum rate. The maximum concentration of X, in turn, is a complex function of temperature^(20).

Assuming that the total activation energy of reaction (2) is less than the activation energy of reaction (3), with the aid of equation (5) it is easy to show that the rate of the hydrocarbon oxidation reaction with increasing temperatu-

passes through a maximum. For this purpose let us rewrite equation (5) in dimensionless coordinates:

$$\theta = \frac{1}{1 + \alpha - \beta}, \tag{6}$$

where $\theta = W \cdot g_1 / W_0 a_3$ is the dimensionless reaction rate; $\alpha = g_2 a_3 / g_1 a_1$ is a dimensionless parameter taking into account the relative rates of processes (3) and (1); $\beta = 2a_2/g_1$ is a dimensionless branching parameter.

Fig. 2

Fig. 2

Figure 2: Fig. 2

Figure 2 presents the curve of the dependence of the reaction rate on temperature, calculated from equation (6). For the calculation it was assumed that $\alpha = 4 \cdot 10^6 e^{-1800/RT}$; $\beta = 9 \cdot 10^4 e^{-10000/RT}$.

We also solved the inverse problem. By specifying the necessary values of the ratio of the pre-exponents and the difference in activation energies of the elementary reactions entering into equation (6), we calculated what the steric factor of reaction (1) should be, with a normal pre-exponent (10^{13}) for reaction (3), in order for the maximum reaction rate to occur at a temperature of 400°. The calculations showed that if the difference in activation energy of reactions (3) and (2) is taken to be 10 kcal/mole, then the steric factor of reaction (1) is of the order of 10^{-3}.

Thus, the proposed simplified scheme of hydrocarbon oxidation, which takes into account the competition between reactions (3) and (2), leads to the appearance of a maximum of the reaction rate with temperature. Obviously, with a further increase in temperature, allowance for reaction (4) will lead to an increase in the reaction rate.

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