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DETERMINATION OF RATE CONSTANTS OF ELEMENTARY REACTIONS OF HYDROGEN ATOMS WITH HYDROCARBONS

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Knowledge of the values of the constants of elementary reactions and of the activation energies of hydrogen atoms with hydrocarbons is of theoretical and practical interest. These reactions play an essential role in the processes of oxidation and cracking of hydrocarbons.

To determine the constant of the reaction

$$H + RH = H_2 + R \qquad (1)$$

and its activation energy, N. N. Tikhomirova and V. V. Voevodskii (^{1}) used the phenomenon of lowering of the second self-ignition limit of hydrogen-oxygen mixtures in the presence of small additions of higher homologues of methane and of certain unsaturated hydrocarbons. A necessary condition for the applicability of this method is the assumption adopted by the authors that the radicals R formed in the course of the reaction, as well as those radicals that may arise as a result of the interaction of R with oxygen, are less reactive than the chain carriers—hydrogen atoms.

The validity of the assumption made above follows from a series of works by Baldwin and co-workers (^{2}), the first of which was carried out independently and simultaneously with work (^{1}).

It follows from the works of Baldwin and co-workers that, in accordance with the generally accepted mechanism of hydrogen oxidation, in hydrogen-rich mixtures there is a linear relationship between the difference in pressures at the second ignition limit of the hydrogen-oxygen mixture, measured in the pure mixture and in the same mixture containing small amounts of saturated hydrocarbons, and the partial pressure of the added hydrocarbons. The weak dependence observed by the authors between the amount of added inhibitor required to lower the second limit by a factor of two relative to the uninhibited limit and the diameter of the reaction vessel and the composition of the mixture apparently occurs only in hydrogen-poor mixtures, in which the leading active centers, along with hydrogen atoms, are also hydroxyl radicals.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The method of inhibiting the second limit for determining constants of elementary reactions has certain shortcomings that make it not very accurate. Even when working under jet conditions it is impossible to exclude the formation of water vapor, whose molecules, as is known (^{4}), are very active third bodies in the chain-termination reaction

$$\mathrm{H} + \mathrm{O_2} + \mathrm{M} = \mathrm{HO_2} + \mathrm{M}.$$

At temperatures of 550-650°C and comparatively high pressures of the reacting mixture, one also cannot neglect the reaction of HO_2 with other molecules, which may lead to the appearance of new chain carriers.

What has been said above, taking into account the difficulties associated with work under jet conditions, somewhat reduces the value of the method for determining constants by

lowering of the upper limit. In this connection we propose a modified version of this method, which makes it possible to determine more accurately the constants and activation energies of atomic hydrogen with various hydrocarbons and substances that are hydrogen donors. The method is based on the displacement (increase) of the lower self-ignition limit of hydrogen-rich mixtures in the presence of hydrocarbons. Working in the kinetic region, one can obtain very low values of the lower limit in the temperature interval 400-530° C. Under these conditions the influence of water vapor, as well as

Fig. 1. Dependence of the ignition limit on temperature. 1 —for the mixture $2H_2 + O_2$; 2 —for a mixture containing 0.6% C_2H_6

Fig. 2. Dependence of the ignition limit on temperature. 1 —for the mixture $2H_2 + O_2$; 2 —for a mixture containing 0.4% C_3H_8

the reaction of HO_2 with other molecules, may be completely neglected. The condition for the lower limit in the presence of an inhibitor is (^{3})

$$2K_2(\mathrm{O_2}) = K_4 + K_5(\mathrm{RH}), \tag{II}$$

where K_2 is the rate constant of the branching reaction $\mathrm{H} + \mathrm{O_2} = \mathrm{OH} + \mathrm{O}$; K_4 is the rate constant of destruction of hydrogen atoms at the walls of the reaction vessel; K_5 is the rate constant of reaction (I).

Fig. 3. H + C2H6. E = 12,000 cal/mole

Figure 3: Fig. 3. H + C2H6. E = 12,000 cal/mole

Equation (II) can be rewritten in the form

$$P_{1O2}^{\mathrm{RH}} = \frac{K_4}{2K_2} + \frac{K_5}{2K_2} P_{\mathrm{RH}}, \tag{III}$$

where $K_4/2K_2$ is the partial pressure of oxygen at the first uninhibited limit; P_{1O2}^{RH} is the partial pressure of oxygen at the first limit in the presence of the inhibitor RH. Hence

$$P_{1O2}^{\mathrm{RH}} = P_{1O2}^{\mathrm{H}_2} + \frac{K_5}{2K_2} P_{\mathrm{RH}}.$$

Denoting the difference $P_{1O2}^{\mathrm{RH}} - P_{1O2}^{\mathrm{H}_2}$ by ΔP and taking into account that the experiments were carried out with a stoichiometric mixture of hydrogen with oxygen, we finally have

$$\frac{\Delta P}{P_{\mathrm{RH}}} = \frac{3}{2}\frac{K_5}{K_2}. \tag{IV}$$

Having determined ΔP from the experimental data, knowing the partial pressure of the inhibitor at the first inhibited limit, as well as the value of K_2, determined earlier in work (^{5}), it is not difficult to calculate, for each temperature, the value of K_5. To determine its temperature dependence, one may use equation (IV), substituting into it, instead of K_5 and K_2, the expressions $K_5 = K_5^0 e^{-E_5/RT}$ and $K_2 = K_2^0 e^{-E_2/RT}$, where E_5 and E_2 are the activation energies of the processes of bulk destruction of hydrogen atoms by reaction (I) and reaction

branching, respectively. Substituting the values of K_5 and K_2 into equation (IV) and taking logarithms, we obtain

$$\lg \frac{\Delta P}{P_{\mathrm{RH}}} = \frac{E_2 - E_5}{2.3RT} + \lg \frac{3K_5^0}{2K_2^0}. \tag{V}$$

From the slope of the straight line in the coordinates $\lg \dfrac{\Delta P}{P_{\mathrm{RH}}} - \dfrac{1}{T}$, one can determine $\Delta E = E_2 - E_5$; hence $E_5 = E_2 - \Delta E$, where $E_2 = 15100$ cal/mole.

Fig. 3. $\mathrm{H} + \mathrm{C_2H_6}$.
$E = 12\,000$ cal/mole

Fig. 4. H + C3H8. E = 8,500 cal/mole

Figure 4: Fig. 4. H + C3H8. E = 8,500 cal/mole

Fig. 4. $H + C_3H_8$.
$E = 8\,500$ cal/mole

The first self-ignition limit of the hydrogen-oxygen mixture was determined by the usual method of rapidly admitting gas into a quartz reactor heated to the required temperature. The reactor was a tube 2.8 cm in diameter and 14 cm long. To obtain low, reproducible values of the limit, the vessel was first washed with hydrofluoric acid and then, after thorough washing with distilled water, treated with a 2% solution of potassium tetraborate. Such treatment of the reactor, combined with repeated flashes in it of an oxygen-rich mixture, made it possible to obtain very low values of the limit, ranging from $P_1 \simeq 0.18$ mm Hg at 410°C to $P_1 \simeq 0.05$ mm at 550°C. Ignitions were recorded with a highly sensitive membrane manometer. The values of the lower limit in the pure mixture $2H_2 + O_2$ and in the same mixture containing 0.6% ethane and 0.4% propane are given in Figs. 1 and 2. To obtain approximately the same displacement in the case of inhibition by butane, experiments showed that only 0.2% butane was required. The values of K_5, calculated for $T = 480°C$ by formula (IV), are given in Table 1.

Table 1

Values of the rate constant of the reaction
$H + RH = H_2 + R$ and activation energies

Hydrocarbon	$K_5 \cdot 10^{13}$, cm^3/molecule · sec	E_5, cal/mole
Ethane	1.49	12000
Propane	2.67	8500
Butane	2.96	6000

To determine E_5, formula (V) was used. It follows from the formula that $\lg \dfrac{\Delta P}{P_{\mathrm{RH}}}$ depends linearly on the reciprocal temperature. Figures 3 and 4 show the experimental data obtained for ethane and propane. As can be seen, all experimental points fall well on the corresponding straight lines. An analogous straight line was also obtained in the case of inhibition of the first limit by *n*-butane. From the slopes of the straight lines, the activation energies of the corresponding reactions $H + RH = H_2 + R$ were determined (see Table 1).

The values obtained for the activation energies of atomic hydrogen with molecules of ethane, propane, and butane somewhat exceed the corresponding values determined in the work of N. N. Tikhomirova and V. V. Voevodskii ([1]), and approach the values calculated by Steacie ([11]) and by many other investigators on the basis of other methods.

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