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Abstract

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THE RATE CONSTANT OF THE REACTION $HO_2 + H_2O = H_2O_2 + OH$

V. A. Poltorak and V. V. Voevodskii (^{1}) showed that in vessels treated with potassium chloride, ignition of a detonating mixture at the third limit is a chain process rather than a thermal one. It had been shown still earlier (^{2}) that in the region of the third ignition limit, along with processes in which H and O atoms and OH radicals participate, an important role is played by the processes $HO_2 + H_2 = H_2O_2 + H$ and $HO_2 + H_2O = H_2O_2 + OH$. From the reaction mechanism one obtains the equation

$$\left[\frac{(p + 6.3p_{H_2O})k_6}{2k_2} - 1\right] \frac{k_7^0}{\left({}^2/_3\, k_8 p + k_9 p_{H_2O}\right)(p + p_{H_2O})} = 1, \qquad (1)$$

where k_2, k_6, $k_7 = k_7^0(p + p_{H_2O})$, k_8 and k_9 are the rate constants of the processes

$$H + O_2 = OH + O \qquad (k_2); \qquad (I)$$

$$H + O_2 + M = HO_2 + M \qquad (k_6); \qquad (II)$$

$$HO_2 \rightarrow \text{destruction at the wall} \qquad (k_7); \qquad (III)$$

$$HO_2 + H_2 = H_2O_2 + H \qquad (k_8); \qquad (IV)$$

$$HO_2 + H_2O = H_2O_2 + OH \qquad (k_9); \qquad (V)$$

p is the sum of the partial pressures of H_2 and O_2, and p_{H_2O} is the partial pressure of H_2O; on the basis of this, from the temperature dependence of the pressure at the third limit p_3, under the assumption that ignition occurs at the moment when the mixture $2H_2 + O_2$ has been practically completely converted into water, i.e., when $p = 0$ and $p_3 = {}^3/_2\, p_{H_2O}$, and also under the assumption that $k_8 \ll k_9$, Poltorak and Voevodskii obtained for the rate constant of process (V)

$$k_9 = 2 \cdot 10^{-16} e^{-8000/RT} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}.$$

Since, however, $E_9 = 8000$ cal/mole is considerably less than the heat of the endothermic process (V), which is about 30,000 cal/mole, Poltorak and Voevodskii came to the conclusion that there exist two forms of the HO_2 radical with different degrees of stability (see also (^{3})). It will be shown below that a more exact calculation, using the same experimental data of Poltorak and Voevodskii, leads to a value of the activation energy of process (V) close to its thermal effect, which removes the question of two forms of the HO_2 radical.

Introducing the initial pressure p_0 of the stoichiometric mixture of H_2 and O_2, related to the pressure p in equality (1) by the relation $p = p_0 - {}^3/{}_2 p_{H_2O}$ (^{1}), from this equality we find

$$p_0^2 - 2\left(a - \frac{3b-4}{4}\, p_{H_2O}\right)/p_0 + \left(c - 9.6\, a p_{H_2O} - \frac{3b-3}{4}\, p_{H_2O}^2\right) = 0,$$

where

$$a = \frac{3}{8}\frac{k_6 k_7^0}{k_2 k_8}, \qquad b = \frac{k_9}{k_8}, \qquad c = \frac{3}{2}\frac{k_7^0}{k_8}.$$

Further, assuming that ignition occurs at some minimum value of p_0 ($p_{0\,\min} = p_3$), determined by the minimum condition

$$\frac{dp_0}{dp_{H_2O}} = 0,$$

from this condition we obtain the following relation between p_3 and p_{H_2O}:

$$p_{H_2O} = \frac{3b-4}{3(b-1)} p_3 - \frac{6.4a}{b-1}.$$

Substituting this value of p_{H_2O} into the preceding quadratic equation, after some transformations we find

$$p_3^2 - 2a\frac{12(5.8b-7.4)}{(3b-2)^2} p_3 + 12\frac{c(b-1) + 4.8 \cdot 6.4a^2}{(3b-2)^2} = 0. \qquad (2)$$

From the data of Wilburn and Hinshelwood (^{4}) it follows (^{3}) that at a temperature of 586°C the constant k_9 is an order of magnitude greater than the

Fig. 1

Figure 1: Fig. 1

constant k_8. Since the experiments of Poltorak and Voevodskii were carried out at temperatures close to this one, we shall take $b = k_9/k_8 \gg 1$. In this case equation (2) can be reduced to the form:

$$\alpha^2 - 2\frac{2.9\frac{k_2}{k_6}p_3 - \frac{k_2^2}{k_6^2}}{5.76}\alpha + \frac{p_3^2}{5.76}\frac{k_2^2}{k_6^2} = 0, \tag{3}$$

where $\alpha = k_7^0/k_9$.

Solving this equation, we find

$$\alpha = \frac{2.9p_3 - \frac{k_2}{k_6}}{5.76}\frac{k_2}{k_6}\left(1 + \sqrt{1 - \frac{5.76p_3^2}{\left(2.9p_3 - \frac{k_2}{k_6}\right)^2}}\right). \tag{4}$$

Fig. 1

Using the data of Poltorak and Voevodskii, we calculated the values of the quantity α for three temperatures covering the entire temperature interval studied by them. In Fig. 1, $\lg \alpha$ is plotted as a function of $1/T$. From the slope of the straight line, for the activation energy of the process $HO_2 + H_2O = H_2O_2 + OH$ one obtains $E_9 = 30$ kcal/mole, i.e., a value practically coinciding with the heat of this reaction, which is about 30 kcal/mole. In view of the fact that the experiments of Poltorak and Voevodskii were carried out in a very narrow temperature interval, the value of E_9 obtained by us may be accurate only to several kilocalories per mole. The lower limit of this quantity is the heat effect of process (V), also known with an accuracy of several kilocalories per mole*. We shall find the upper limit by adding to the heat of reaction the activation energy of the reverse process E_9' $(OH + H_2O_2 = H_2O + HO_2)$. The latter quantity can be estimated in the following way. Frost and Oldenberg (^{7}) found that OH radicals formed in a discharge in H_2O_2 disappear in approximately 0.01 sec. Assuming that the rate of disappearance of hydroxyl is determined by the rate of the process

$$OH + H_2O_2 = H_2O + HO_2$$

and that during the time $t = 0.01$ sec the concentration of OH decreases by a factor of 10, from the formula

$$\frac{[OH]}{[OH]_0} = e^{-k_9'(H_2O_2)t}$$

* On the basis of tabulated data (5) and the following values of dissociation heats: $D_{\mathrm{O-H}} = 102.4$ kcal/mole and $D_{\mathrm{O_2-H}} = 47 \pm 4$ kcal/mole, and the enthalpy of formation of H_2O_2, $\Delta H_{298} = 32.5$ kcal/mole (6), for the heat of the process $HO_2 + H_2O = H_2O_2 + OH$ under standard conditions we find -29.6 ± 4.5 kcal/mole.

we find for the rate constant of this process $k_9 = 10^{-14}$ $\mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}$ ($p_{H_2O_2} = 1$ mm Hg, $T = 400$°K). Representing the quantity k_9' in the form $k_9' = k_9^{0\prime} e^{-E_9'/RT}$ and assuming that the preexponential factor $k_9^{0\prime}$ cannot exceed 10^{-11} $\mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}$, for the upper limit of E_9' we obtain $E_9' = 5$ kcal/mole. Thus, the upper limit of E_9 can hardly exceed $30+5 = 35$ kcal/mole.

Calculating from the values of α obtained by us the quantity $k_7^0 : k_9^0 = -2.3 \cdot 10^{13}$ $\mathrm{cm^3 \cdot molecule^{-1}}$ ($E_9 = 30000$ kcal/mole) and taking $k_7^0 = 700$ $\mathrm{sec^{-1}}$*, we find $k_9^0 = 3 \cdot 10^{-11}$ $\mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}$ and, consequently,

$$k_9 = 3 \cdot 10^{-11} e^{-30000/RT} \ \mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}.$$

Let us also calculate the quantity $b = k_9 : k_8$. Substituting here the value of k_9 found by us together with the value k_8, expressed by the approximate formula $k_8 = 2 \cdot 10^{-13} e^{-24000/RT}$ $\mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}$ (3), for the temperature 586° we obtain $b = 5$ instead of $b = 11$, obtained from the data of Willbourn and Hinshelwood (3,4).

In conclusion we shall touch upon the following question. Above it was assumed that the constant k_8 corresponds to process (IV), whose heat effect is −15 kcal/mole. In addition to this process, however, the exothermic process

$$HO_2 + H_2 = H_2O + OH \qquad \text{(IV')}$$

with a heat effect of +53 kcal/mole is possible.

It can be shown that, when both these processes are taken into account, equation (1) will not change its form, and only instead of the constant k_8 we shall have the sum $k_8 + k_8'$.

The available experimental data are insufficient to decide whether both constants or only one of them should enter this equation (in the temperature interval studied). With the endothermicity of process (IV) equal to 15 kcal/mole, an activation energy of 24 kcal/mole appears quite acceptable. On the other hand, process (IV′), proceeding with rupture of two bonds (H—H and HO—O), despite its large exothermicity, must possess a considerable activation energy and a small steric factor, which must likewise be regarded as compatible with the constant

$$k_8 \ (\text{or } k_8') = 2 \cdot 10^{-13} e^{-24000/RT} \ \mathrm{cm^3 \cdot molecule^{-1} \cdot sec^{-1}}.$$

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* This number was obtained on the basis of the formula

$$k_7^0 = \frac{39.9 D_1}{d^2},$$

where D_1 is the diffusion coefficient at a pressure of 1 mm Hg and d is the diameter of the spherical reaction vessel ($d = 4$ cm). The diffusion coefficient of the HO_2 radical was set equal to the diffusion coefficient of O_2, which at normal temperature and pressure is 0.2 cm^2/sec.

Note: Figure translations are in progress. See original paper for figures.

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