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Abstract

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Activation Energy of the Elementary Reaction $RO_2 + RH$ in the Oxidation of n-Decane

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At present there are no direct methods for studying the elementary stages of liquid-phase hydrocarbon oxidation processes. However, in recent years some information on the elementary oxidation reactions of liquid hydrocarbons has been obtained from data on oxidation kinetics ([1]), by applying the method of photochemical aftereffect ([2,3]) and the rotating-sector method ([4]). All these results pertain to the initial stages of hydrocarbon oxidation, when the only product present in the system is the primary oxidation product—hydroperoxide.

In all cases, in treating the experimental data it was considered proven that the formation of hydroperoxide proceeds by a chain mechanism according to the scheme:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \tag{1}$$

$$RO^{\cdot} + RH \rightarrow RO_2H + R^{\cdot} \tag{2}$$

In particular, it follows from this scheme that, at a sufficiently high oxygen pressure, when recombination of RO_2 radicals becomes the principal type of chain termination, the oxidation rate is equal to ([5])

$$w = w_i^{1/2} \frac{k_2}{k_3^{1/2}} [RH], \tag{3}$$

where w_i is the rate of initiation, k_2 is the bimolecular rate constant of the chain-propagation reaction, and k_3 is the rate constant for recombination of RO_2 radicals. The criterion for the applicability of formula (3) is the absence of a dependence of the oxidation rate on the partial pressure of oxygen in the gas phase over the investigated pressure range. Knowing the rate of initiation and determining the oxidation rate, we can use formula (3) to calculate the ratio $k_2/k_3^{1/2}$ and the temperature dependence of this ratio, i.e., the quantity $E_2 - \frac{1}{2}E_3$. Since E_3 is the activation energy of the recombination process of

Fig. 1. Kinetic curve of peroxide accumulation during oxidation of n-decane at 130° with oxygen (a) and with a 1:1 mixture of oxygen and nitrogen (b).

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two radicals, apparently close to zero, this makes it possible to determine the activation energy of process (2).

In the present work we attempted to apply an analogous procedure to determine the value of E_2 in the oxidation reaction of n-decane. The difficulty of the problem consisted in the fact that, in the oxidation of n-decane, peroxide can no longer be regarded as the only oxidation product, since along with it, from the very beginning of oxidation, compounds with other functions—alcohols, carbonyl compounds, acids, and esters—are present in comparable amounts ([6]). However, in previous studies on the oxidation of n-decane it was established that all these products are formed as a result of the decomposition of hydroperoxides, i.e., the first stage of the process in the oxidation of n-decane, just as in the oxid—

in the oxidation of hydrocarbons of other classes is the formation of hydroperoxide. The main difference in the oxidation of n-decane is that the formation of hydroperoxide by reaction (2) is, already at the early stages of oxidation, substantially superimposed by the process of hydroperoxide decomposition. The decomposition of peroxides proceeds according to a monomolecular law with activation energy $E = 24$ kcal ([7]), and, consequently,

$$w = \frac{d[\mathrm{ROOH}]}{dt} = k_2[\mathrm{RO_2}][\mathrm{RH}] - k_4[\mathrm{ROOH}], \tag{4}$$

where k_4 is the monomolecular rate constant for peroxide decomposition.

Oxidation of hydrocarbons is a chain process with pronounced chain branching. The autocatalytic character of the oxidation of n-decane shows that it is not an exception in this respect. The pronounced branching is due, as is now generally accepted, to the decomposition of hydroperoxide molecules into two free radicals:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH}. \tag{5}$$

Fig. 1. Kinetic curve of peroxide accumulation during oxidation of n-decane at 130° with oxygen (a) and with a $1:1$ mixture of oxygen and nitrogen (b).

The activation energy of this reaction for the case of decyl hydroperoxide was determined by Twigg and was found to be $E_5 = 31.7$ kcal ([8]). In this connection it should be borne in mind that the rate constant of reaction (5), k_5, of course does not coincide with the quantity k_4, since decomposition according to scheme (5) is not the only path of peroxide decomposition.

Assuming that the rates of initiation and chain termination are practically equal, and considering that termination occurs mainly by recombination of RO_2 radicals, we obtain:

$$k_5[\mathrm{ROOH}] = k_3[\mathrm{RO_2}]^2, \tag{6}$$

which makes it possible to transform equation (4) into the form

$$w = k_2\sqrt{\frac{k_5}{k_3}}\,[\mathrm{RH}]\sqrt{[\mathrm{ROOH}]} - k_4[\mathrm{ROOH}].$$

The maximum rate of peroxide accumulation is determined from the condition

$$\frac{dw}{dt} = 0$$

or, equivalently,

$$\frac{dw}{d[\mathrm{ROOH}]} = 0,$$

since

$$d[\mathrm{ROOH}]/dt > 0$$

(in the region of the kinetic curve that is of interest to us). Hence we obtain

$$w_{\max} = \frac{k_2^2 k_5[\mathrm{RH}]^2}{4k_3k_4},$$

or, for the effective activation energy of oxidation E, determined from the temperature dependence,

$$E = 2E_2 + E_5 - E_3 - E_4. \tag{7}$$

Since the quantities E_4 and E_5 are known, while E_3, as the activation energy of recombination, should be close to zero, determination of the value of E makes it possible to calculate E_2—the activation energy of the elementary reaction $RO_2 + RH$ in the oxidation of n-decane.

The oxidation of n-decane was carried out in an oxidation cell described in our earlier works ([6]). In order to verify the correctness of the -

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

tion of the preferential chain termination by recombination of the radicals RO_2, we recorded kinetic curves for the accumulation of peroxides during the oxidation of n-decane at 130° at two different partial pressures of oxygen: 1 and 0.5 atm (the latter was produced by blowing through n-decane, instead of pure oxygen, a mixture of oxygen with nitrogen in the ratio 1:1). The corresponding results are presented in Fig. 1. It is seen that the formation of peroxides in a stream of oxygen and in a stream of a mixture of oxygen with nitrogen proceeds at one and the same rate. This confirms the validity of condition (6), since only in cases of chain termination by recombination of the radicals RO_2 does the rate of oxidation not depend on the oxygen pressure.

In Fig. 2 are shown the kinetic curves for the accumulation of peroxides during the oxidation of n-decane at different temperatures. In Fig. 3, in Arrhenius coordinates, is shown the dependence of the maximum rate of peroxide accumulation on temperature. From this dependence, for the total activation energy one obtains the value $E = 31$ kcal, which according to relation (7) gives the value 11.5 kcal for E_2.

Fig. 2. Kinetic curves for the accumulation of peroxides during the oxidation of n-decane by oxygen at different temperatures: a —150°, b —140°, v —130°, g —120°

In order to find out how plausible such a value of E_2 is, let us estimate this quantity theoretically by Polanyi' s formula. According to this formula for an endothermic reaction ([9]),

$$E = |q| + 11.5 - 0.25|q|,$$

where q is the heat effect of the reaction.

Fig. 3. Dependence of the maximum rate of peroxide accumulation on temperature

For reaction (2) the heat effect is equal to the difference between the dissociation energies of the OH bond in the hydroperoxide and of the CH bond in the initial hydrocarbon.

The dissociation energy of the secondary CH bond in n-decane, which is predominantly oxidized ([10]), should not differ appreciably from the same value for propane. According to the data given in Cottrell' s monograph, this value is

94 kcal. The energy of the OH bond in decyl hydroperoxide should not differ appreciably from the same value for hydrogen peroxide, since the residue R in the hydroperoxide can scarcely exert a substantial influence on the OH bond, separated from it by two simple bonds. For hydrogen peroxide,

$$q_{\mathrm{H-O_2H}} = q_{\mathrm{HO-OH}} + 2q_{\mathrm{O-H}} - q_{\mathrm{O=O}} - q_{\mathrm{H-O_2}}.$$

The necessary values of the dissociation energies are found in Cottrell' s monograph ([11]) ($q_{\mathrm{HO-OH}} = 48$ kcal, $q_{\mathrm{O-H}} = 103$ kcal, $q_{\mathrm{O=O}} = 117$ kcal) and in the work of Foner and Hudson ([12]) ($q_{\mathrm{H-O_2}} = 47$ kcal), whence the dissociation energy of the OH bond in hydrogen peroxide is obtained as equal to 90 kcal.

Calculation by Polanyi' s formula with the above-adopted values of the OH and CH bond energies gives $E_2 = 14.5$ kcal. Taking into account the approximate character of Polanyi' s formula and the uncertainties in the bond-energy values, the information obtained should be regarded as satisfactory. It should also be noted that if the dissociation energy of the C–H bond is taken as 89 kcal[9] (instead of 94 kcal), the calculation gives $E_2 = 11.5$ kcal, i.e., it agrees well with the experimental data.

Table 1

Comparison of the activation energies of the reaction $\mathrm{RO_2} + \mathrm{RH}$, obtained from experimental data and calculated by Polanyi' s formula

Hydrocarbon	Activation energy, from kinetic data	Activation energy, by Polanyi
Ethyl linoleate ([1])	4	5
Tetralin ([2])	4.3	6.5
Squalene ([1])	7	7
Methyl oleate ([1])	8	7
n-Decane	11.5	14.5

It is of interest to test how generally Polanyi' s formula is applicable to reactions of this kind. In Table 1, the first column gives the values of E_2 (the activation energy of the reaction $\mathrm{RO_2} + \mathrm{RH}$) found by various authors from kinetic data using formula (3) (including the values for *n*-decane obtained in the present work). The second column gives the values of E_2 calculated for the same hydrocarbons by Polanyi' s formula (the value of the C–H bond dissociation energy is taken from data for simpler hydrocarbons of the same structure).

As is seen from Table 1, the Polanyi relation for hydrocarbons of different classes gives values of the activation energies of the elementary reaction $\mathrm{RO_2} + \mathrm{RH}$ that agree well with those found from experimental data.

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