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Abstract

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A NEW REACTION OF CHAIN INITIATION IN LIQUID-PHASE OXIDATION

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The rate of oxidation as a chain process depends on the rate of formation of free radicals. In a developed reaction, the formation of free radicals occurs mainly at the expense of molecular intermediate products, in particular hydroperoxides. Compared with developed oxidation, the rate of chain initiation at the initial moment of the reaction is tens and hundreds of times smaller and is of the order of magnitude $10^{-9} \div 10^{-8}$ mol/l $\cdot$ sec. The initial rate of chain initiation determines the duration of the induction period.

At the initial moment of the reaction, in the absence of initiating agents, chain initiation can occur only at the expense of the starting substance RH and dissolved oxygen. Free radicals can in principle be formed by slow dissociation of the starting substance along the weakest bonds, for example C—C bonds, whose rupture energy is 60-80 kcal/mol. The rate of formation of free radicals due to dissociation of a substance with bond energy 60 kcal/mol is 10^{-18} mol/l $\cdot$ sec ($t = 140^{\circ}$, [RH] = 10 mol/l), i.e., very small. With rare exceptions, dissociation of the starting substance cannot serve as any significant source of free radicals in oxidation reactions.

The bimolecular reaction between RH and O_2

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot - q_1 \qquad (1)$$

is at present a generally recognized source of free radicals at the initial moment of thermal oxidation ([1]). If this is indeed so, then the reaction $RH + O_2$ must provide such rates of formation of free radicals as are observed experimentally. The values W_0, determined by the inhibition method ([2]), are known for a number of substances (Table 1).

Table 1

Rates of chain initiation in liquid-phase oxidation reactions

Substance	Temp., °C	W_0, mol/l · sec	E_0, kcal/mol	Lit. source
Benzaldehyde	5	$3.5 \cdot 10^{-8}$	11.6 ± 1.5	([3])
Decanal	5	$5 \cdot 10^{-9}$	15.6 ± 1	([4])
Cyclohexane	140	$4.6 \cdot 10^{-8}$		([2])
n-Decane	130	$1.3 \cdot 10^{-8}$		([5])
Tetralin	110	$5.7 \cdot 10^{-7}$		([6])
Cyclohexanol	120	$2.7 \cdot 10^{-8}$	33.5 ± 1.5	

Let us estimate the rates of chain initiation by reaction (1) and compare them with the experimental values. The endothermicity of reaction (1) is equal to $q_1 = Q_{\mathrm{R-H}} - Q_{\mathrm{H-O_2\cdot}}$, $Q_{\mathrm{H-O_2\cdot}} = 47$ kcal/mol ([1]), and $q_1 = (Q_{\mathrm{RH}} - 47)$ kcal/mol. The energy

activation energy $E = q_1 + \varepsilon \approx q_1$, since ε is apparently small. The steric factor for bimolecular reactions in the liquid phase is of the order of 10^{-3}–10^{-5}. In our calculations we shall take the steric factor to be 10^{-3}. The rate constant of reaction (1) is equal to $10^{11} \cdot 10^{-3} \exp(-q_1/RT) = 10^8 \exp(-q_1/RT)$ l/mole · sec, and the rate of radical formation by this reaction is

$$W_0 = 2 \cdot 10^8 \exp(-q_1/RT)[\mathrm{RH}][\mathrm{O_2}] \text{ mole/l} \cdot \text{sec}.$$

To calculate the rate it is necessary to know the strength of the bond being broken, $Q_{\mathrm{R-H}}$, $[\mathrm{O_2}]$, and [RH].

In the case of benzaldehyde, the energy of the C–H bond in the aldehyde group is 78 kcal/mole ([7]), [RH] = 2 mole/l, $[\mathrm{O_2}] = 4 \cdot 10^{-3}$ mole/l, $t = 5°$, $q_1 = 78 - 47 = 31$ kcal/mole,

$$W_0 = 2 \cdot 10^8 \exp(-31000/RT) \cdot 2 \cdot 4 \cdot 10^{-3} = 10^{-18} \text{ mole/l} \cdot \text{sec}.$$

For decanaldehyde $Q_{\mathrm{R-H}}$ may be taken to be the same as in acetaldehyde, where $Q_{\mathrm{R-H}} = 80$ kcal/mole ([7]), [RH] = 5, $[\mathrm{O_2}] = 4 \cdot 10^{-3}$, $t = 5°$, $q_1 = 80 - 47 = 33$ kcal/mole, $W_0 = 6 \cdot 10^{-20}$ mole/l · sec. In cyclohexane the strength of the C–H bond will be taken as 88 kcal/mole, and the steric factor as 10^{-2}, since 12 C–H bonds can take part in the reaction; [RH] = 10, $[\mathrm{O_2}] = 10^{-1}$, $t = 140°$, $q_1 = 88 - 47 = 41$ kcal/mole, $W_0 = 5 \cdot 10^{-13}$ mole/l · sec. For *n*-decane $Q_{\mathrm{R-H}} = 89$ kcal/mole, [RH] = 5, $[\mathrm{O_2}] = 10^{-2}$, $t = 130°$, $q_1 = 89 - 47 = 42$ kcal/mole. The steric factor, as in the case of cyclohexane, will be taken equal to 10^{-2}, $W_0 = 2 \cdot 10^{-15}$ mole/l · sec. The strength of the α C–H bond in tetralin may be taken to be the same as in ethylbenzene ([8]), $Q_{\mathrm{R-H}} = 75$ kcal/mole, [RH] = 7, $[\mathrm{O_2}] = 10^{-2}$, $t = 110°$, $q_1 = 75 - 47 = 28$ kcal/mole, $W_0 = 2 \cdot 10^{-10}$ mole/l · sec. In cyclohexanol $Q_{\mathrm{R-H}} \approx 85$, $W_0 = 2 \cdot 10^{-14}$ mole/l · sec.

The calculated values of W_0 should be regarded as approximate. It should be kept in mind that in the calculations minimal values for E ($\varepsilon = 0$) were deliberately taken, as well as a reasonably maximal value for the steric factor f_1. Thus reasonably maximal values were obtained for W_0, which nevertheless proved to be 5-10 orders of magnitude smaller than the experimental values of W_0. Such an enormous discrepancy between experiment and calculation cannot be the result of errors in estimating the values of E and f_1; it indicates the existence, in the initial system $RH + O_2$, of another, far more powerful source of free radicals.

Such a source of formation of free radicals may be a trimolecular reaction between the initial substance and oxygen:

$$RH + O_2 + HR \rightarrow R\cdot + H_2O_2 + R\cdot - q_2. \tag{2}$$

$$q_2 = 2Q_{R-H} - Q_{H-H} + \Delta H_{H_2O_2}, \quad Q_{H-H} = 103 \text{ kcal/mole}.$$

The value $\Delta H_{H_2O_2}$ deserves special discussion. Strictly speaking, it is necessary to consider the formation of hydrogen peroxide in the given solvent RH, where the enthalpy of formation of hydrogen peroxide is equal to $\Delta H_{H_2O_2(gas)} + \Delta H_{soln}$. Since the heat of dissolution of H_2O_2 in organic solvents is unknown, as a first approximation one may take the heat of formation of liquid hydrogen peroxide, $-\Delta H_{H_2O_2(l)} = 45$ kcal/mole, subtracting the heat of formation of the hydrogen bond, 4 kcal/mole; $q_2 = 2(Q_{R-H} - 72)$ kcal/mole. It is not hard to see that reaction (2) is energetically much more favorable than reaction (1). For example, for $Q = 90$ kcal/mole, $q_1 = 43$ kcal/mole, whereas $q_2 = 36$ kcal/mole; for $Q = 80$ kcal/mole, $q_1 = 33$ kcal/mole, whereas $q_2 = 16$ kcal/mole.

Trimolecular collisions in the liquid phase are practically as frequent as bimolecular ones: the ratio of the number of bimolecular collisions to trimolecular collisions is

$$\frac{10^{11}[RH][O_2]}{10^{10}[RH]^2[O_2]} = \frac{10}{[RH]};$$

at [RH] = 2 mole/l it is equal to 5, and at [RH] = 10 mole/l it is equal to 1. The energetic favorability of reaction (2) and the high frequency of trimolecular collisions in the liquid phase lead to the result that the rate of reaction (2), as a rule, is much higher than the rate of reaction (1).

Let us compare the rate of the trimolecular reaction with the experimental values of W_0. The activation energy $E = q_2 + \varepsilon \simeq q_2$. The steric factor for the trimolecular reaction will be smaller than for the bimolecular one. As is known, the steric factor expresses the probability that, in the energy-rich molecules that have collided, a certain part of this energy (greater than E) is localized

in the bonds broken in the elementary act. Simultaneous localization of energy in two C–H bonds in two RH molecules colliding with O_2 is a complex event. The probability of such an event is equal to the product of the probabilities of energy localization in each of the reacting C–H bonds. Therefore

Table 2

Comparison of experimental and calculated values of W_0 (mol/l · sec)

Substance	W_0 from experiment	W_0 by reaction (1)	W_0 by reaction (2)
Benzaldehyde	$3.5 \cdot 10^{-8}$	10^{-18}	$8 \cdot 10^{-7}$
Decanal	$5 \cdot 10^{-9}$	$6 \cdot 10^{-20}$	$4 \cdot 10^{-9}$
Cyclohexane	$4.6 \cdot 10^{-8}$	$5 \cdot 10^{-13}$	10^{-9}
n-Decane	$1.3 \cdot 10^{-8}$	$2 \cdot 10^{-15}$	$8 \cdot 10^{-13}$
Cyclohexanol	$2.7 \cdot 10^{-8}$	$2 \cdot 10^{-14}$	$3 \cdot 10^{-10}$

in the first approximation one may set $f_2 = f_1 \cdot f_1 = f_1^2$. Since we took $f_1 = 10^{-3}$, then $f_2 = 10^{-6}$ (and 10^{-4} for decane and cyclohexane). The rate of the trimolecular reaction is

$$W_0 = f_2 \cdot 2 \cdot 10^{10} \exp(-E_2/RT)\,[\mathrm{RH}]^2[O_2].$$

The quantities $Q_{\mathrm{R-H}}$, $[O_2]$, [RH], and t are the same as in the preceding calculations. The calculated values of W_0 are compared in Table 2 with the experimental data and with the values of W_0 for reaction (1).

Examination of Table 2 shows that the values of W_0 calculated for the reaction $2\mathrm{RH} + O_2$ do not differ greatly from the experimental values (only by 1-2 orders of magnitude, and only in the case of decane by 5 orders). It should be borne in mind here that the values of W_0 calculated for reaction (2) are highly sensitive to the deviation of the values of Q_{RH} and f_2 accepted by us from the true ones. An error in $Q_{\mathrm{R-H}}$ of 2 kcal/mol leads to an error in E of 4 kcal/mol and to an error in W_0 of 2 orders of magnitude. The range of variation of f_2 lies from 10^{-3} to 10^{-12}. Therefore, taking into account the approximate nature of the calculation, the discrepancy between experiment and calculation of only 1-2 orders of magnitude should be regarded as good agreement. Attention should also be paid to the fact that the values of W_0 calculated for reaction (2) are in some cases larger (benzaldehyde), and in others smaller, than in experiment. Moreover, reaction (2) gives values of E that practically coincide with the experimental values for benzaldehyde and decanaldehyde.

The kinetic data on the proportionality between the initial rate of oxidation and $[\mathrm{RH}]^2$ ([6,9]) are in good agreement with the trimolecular mechanism of chain initiation. The rate of oxidation, as is known, is $V_0 = k[\mathrm{RH}][\mathrm{RO}_2\cdot]$; with

quadratic chain termination $[RO_2\cdot] \sim W_0^{1/2}$; for reaction (2), $W_0 \sim [RH]^2$, whence $V_0 \sim [RH]^2$. In some cases a dependence $V_0 \sim [RH]^{3/2}$ is observed, which at first sight speaks in favor of reaction (1). However, exactly the same dependence will also be observed when chains are initiated by an impurity of a substance (for example, a peroxide) decomposing into free radicals.

Summarizing all that has been said above, it should be emphasized that the trimolecular reaction $2RH + O_2$ proposed in the present work is in good agreement with the available experimental data. There is every reason to believe that it is this reaction, and not the reaction $RH + O_2$, that is the principal source of free radicals at the initial moment of liquid-phase oxidation. Very

it is probable that, in the case of substances with easily cleaved C–H bonds (aldehydes, 1,4-diene hydrocarbons, 1,3-diphenylalkanes), this reaction remains the main source of free radicals even in developed oxidation, successfully competing at low temperatures with the formation of free radicals from peroxides.

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