KINETIC PRINCIPLES OF THE INITIATED OXIDATION OF OLEFINS OF THE BICYCLO[2.2.1]HEPTENE SERIES

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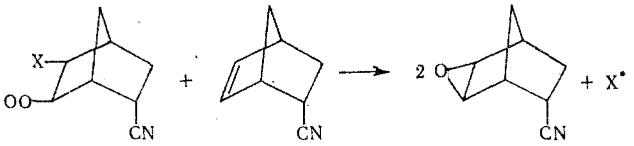
The oxidation of olefins of the bicyclo[2.2.1]heptene series (substituted norbornenes) leads to the formation of oxides of the corresponding olefins with a yield of 80 mole % of the reacted olefins [1, 2]. Such a high yield of the olefin oxide cannot be explained within the framework of the known mechanisms of the epoxidation of olefins in oxidation by molecular oxygen [3-6].

For the epoxidation of norbornene derivatives, a mechanism has been proposed [1], including the step



where X is a peroxide radical of the initiator or a nitrile of bicyclo[2.2.1]hepten-5-oic endo(exo)-acid.

The peculiarities of nitriles of bicyclo[2.2.1]hepten-5-oic endo-(I) and exo-acids (II) — Bayer stress of the valence angles, leading to activation of the double bond, and a low probability of stripping of hydrogen atoms in the α position to the double bond [1, 7] — do not permit the use of the usual concepts [8] of the mechanism of the interaction of radicals formed from the initiator with the initial olefin, without supplementary investigation.

It might have been assumed that radicals of the initiator are initially added at the double bond of the olefin — the most reactive site of the molecule under conditions of oxidation. If the initiator radicals are added at the double bond of the olefin and participate in an epoxidation reaction leading to the regeneration of these radicals, then they should have participated in the reactions of chain termination and, consequently, the rate of oxidation of (I) and (II) should depend on the nature of the initiator used. To test this hypothesis we compared the kinetic principles of the oxidation of (II) in the presence of initiators — azoisobutyrodinitrile (AIBN) and benzoyl peroxide (BP). For the same purpose we used the method of chemiluminescence to compare the reactions of chain termination in systems of AIBN—chlorobenzene (CB) and AIBN—CB—(I) and in the joint oxidation of (I) and ethylbenzene (EB).

EXPERIMENTAL METHOD

The oxidation of (I) and (II) and the joint oxidation of (I) with isopropylbenzene (IPB) and EB was conducted in a blubber-type reactor with a reflux condenser and a capillary for collection of samples at 75-90° in CB in the presence of AIBN. In a comparison of the rates of oxidation of (II) in the presence of various initiators, AIBN and BP were taken in amounts of providing for constancy of the rates of initiation. The rate of absorption of O_2 was measured on a manometric setup. The luminescence intensity in the system

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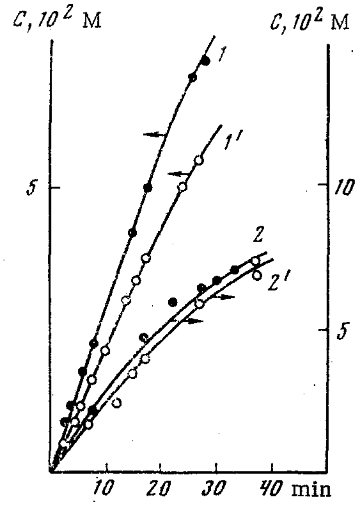


Fig. 1

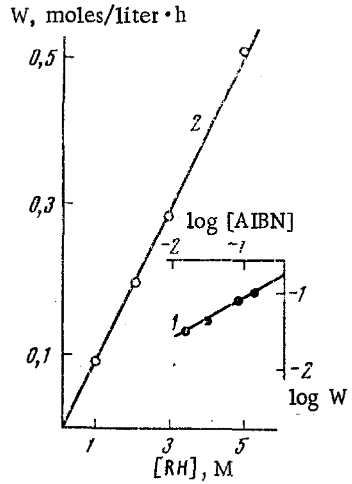


Fig. 2

Fig. 1. Kinetic curves of the absorption of oxygen (1, 1') and accumulation of the oxide (II) (2, 2') in the oxidation of (II) (3 M in chlorobenzene) at 84° in the presence of initiators: 1,2) benzoyl peroxide, $5.3 \cdot 10^{-2}$ M; 1',2') AIBN, 10^{-2} M. Rate of initiation $2.6 \cdot 10^{-6}$ mole/liter·sec.

Fig. 2. Dependence of the rate of absorption of oxygen in the oxidation of (I) in chlorobenzene solution on the concentration of the initiator (1) and the initial olefin (2): 1) (I), 2 M 75° (logarithmic coordinates); 2) (I), 3 M, 10^{-2} M AIBN, 90°.

AIBN—CB and AIBN—CB—(I) and in the joint oxidation of (I) and EB was measured on a chemiluminescence setup designed at the Institute of Chemical Physics, Academy of Sciences of the USSR; experiments were conducted at 75°, and the reaction mixture was continuously saturated with air.

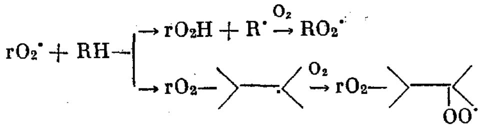
The oxides (I) and (II) were analyzed by the method of gas—liquid chromatography; the stationary phase was a mixture of apiezon L and distearate (15 and 5% of the weight of the solid carrier, respectively), applied on Celite C-545, 150°.

DISCUSSION OF RESULTS

The initial rates of absorption of O_2 in the oxidation of (II) in the presence of AIBN and BP differ by 20%, while the rates of oxidation of the oxide (II) practically coincide (Fig. 1). The difference of the rates of absorption of O_2 in the presence of AIBN and BP may be associated with the fact that the real rates of initiation in our case differ from the values found on the basis of the data [9].

The absence of an influence of the nature of the initiator on the rate of absorption of O_2 and the rate of formation of the oxide (II) is evidence that the radicals formed from the initiator do not participate in the recombination reaction, and evidently there is practically a complete exchange of these radicals for the radicals of the initial olefin. This conclusion is confirmed by the chemiluminescence method. When small quantities of (I) are added to a solution of 10^{-3} M AIBN in CB in the presence of $5 \cdot 10^{-4}$ M dibromoanthracene (or in the absence of an activator), rapid exchange of initiator radicals for olefin radicals is accompanied by a sharp increase in the chemiluminescence intensity and a cessation of the increase in the luminescence intensity at concentrations of (I) of 0.1 M, analogously to that observed for other hydrocarbons [10].

Considering that peroxide radicals of substituted norbornene participate in recombination and assuming the mechanism of epoxidation suggested earlier [1], the complete scheme of oxidation of (I) and (II) can be represented as follows:



(1)

(1')

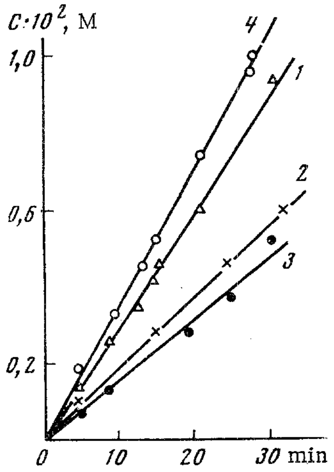
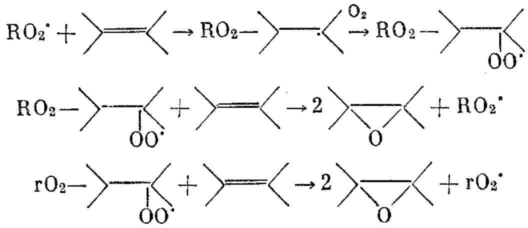


Fig. 3. Kinetic curves of the accumulation of the oxide (I) in the oxidation of (I) in various solvents, 80°, AIBN concentration 10^{-2}, (I) 1.0 M: 1) in chlorobenzene; 2) in a 50% mixture of chlorobenzene and ethylbenzene; 3) in ethyl benzene; 4) in isopropylbenzene.

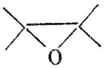


(2)

(3)

(3')

$$2RO_2^\cdot \rightarrow \text{Recombination} \qquad (6)$$

where RH (or $>=<$) represents (I) or (II);  represents the oxide of (I) or (II); rO_2 represents peroxide radicals of the initiator AIBN.

The method of equilibrium concentration leads to the following expression for the rate of absorption of O_2 and the formation of the olefin oxide:

$$W_{O_2} = \left(\frac{3}{2} + \frac{k_1'}{k_1}\right) W_i + k_2/\sqrt{k_6}\, W_i^{1/2}[\mathrm{RH}] \qquad \text{(I)}$$

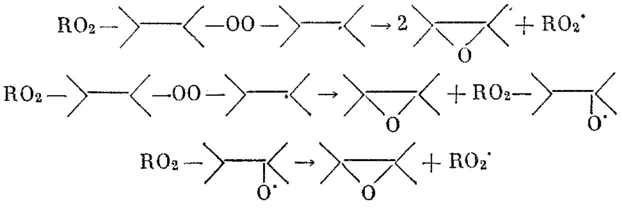
$$W_{\text{oxide}} = 2\,\frac{k_1'}{k_1}\, W_i + 2k_2/\sqrt{k_6}\, W_i^{1/2}[\mathrm{RH}] \qquad \text{(II)}$$

Since oxides are the basic oxidation products of (I) and (II), the scheme does not consider polymerization reactions, which, as is believed, parallel the formation of the olefin oxide [11].

The dependence of the rate of oxidation of (I) on the olefin concentration in the region of concentrations 1-5 M is described by a first-order equation (Fig. 2), which corresponds to Eq. (2), obtained for the oxidation scheme if the first member of expression (1) is negligible in comparison with the second. In the case of sufficiently long chains (10 links), this can be only in the case when $k_1'/k_1 < 1$. This condition is fulfilled if the initiator radicals react with (I) or (II) primarily according to a reaction of stripping of hydrogen [reaction (1)]. Then further conversions of the radical $rO_2 - > - < -OO^\cdot$ [in particular, reaction (3')] can be neglected, leaving only the second factor in expression (2).

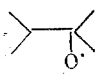
As can be seen from Fig. 2, the rate of absorption of O_2 in the oxidation of (I) is proportional to the rate of initiation to the exponent 0.55. This corresponds to a scheme of oxidation with quadratic chain termination [8]. The rate of generation of chains on molecules of (I) can be neglected, since this quantity, measured according to the rate of consumption of neozone D, is only $1.1 \cdot 10^{-8}$ mole/liter·sec, while under conditions of initiated oxidation of (I) the rates of initiation lie within the range $0.8 \cdot 10^{-6}$-$6 \cdot 10^{-6}$ mole/liter·sec (the initial rates of initiation are compared).

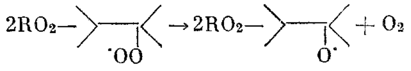
Step 3, leading to the formation of the basic oxidation product – the oxide (I) – is on the whole an energetically profitable event, with an exothermic effect of ~7 kcal. This reaction can proceed through the formation of an intermediate radical, for which two pathways of transformation can be considered:



(a)

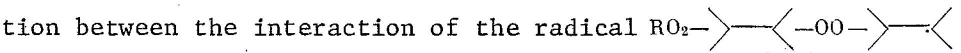
(b)

The oxy radicals RO_2–  can also arise in the interaction of two peroxide radicals [12]



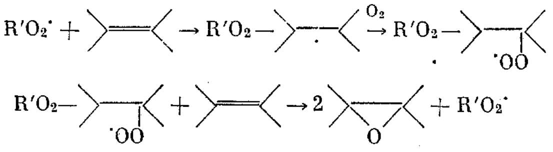
(c)

The introduction of reaction (c) into the oxidation scheme does not lead to any change in the appearance of expressions (I) and (II). Evidently, with increasing olefin concentration the relative role of reaction (c) in the summary mechanism of the process should be reduced.

The increase in the yield of the olefin oxide in the case of a decrease in the O_2 concentration [13] does not contradict the accepted scheme and cannot be explained by competition between the interaction of the radical  with O_2 and its conversion to an olefin oxide [3]. Thus, the reaction sequence (1)-(6) accepted describes the experimentally observed kinetic principles of the oxidation of (I) and (II).

Since it can be considered within the framework of the accepted mechanism that aklyl peroxide radicals of (I) and (II) participate in the formation of the epoxidizing agent, it was necessary to verify what changes cause the replacement of these radicals by peroxide radicals of a different hydrocarbon. The scheme of the joint oxidation of (I) (RH in the scheme) and a second hydrocarbon (R'H) includes not only the reaction sequence (1)-(6) but also reactions of crossed chain propagation and termination [14, 15] and a step of epoxidation (3"), in which peroxide radicals of the hydrocarbon R'H participate:

$$rO_2' + R'H \rightarrow rO_2H + R'' \xrightarrow{O_2} R'O_2^{\cdot} \qquad (1")$$



(2')

(3")

$$R'O_2 + RH \rightarrow R'O_2H + R^{\cdot} \xrightarrow{O_2} RO_2^{\cdot} \qquad (4)$$

$$RO_2 + RH \rightarrow RO_2H + R^{\cdot} \xrightarrow{O_2} RO_2^{\cdot} \qquad (4')$$

$$R'O_2 + R'H \rightarrow R'O_2H + R'' \xrightarrow{O_2} R'O_2^{\cdot} \qquad (5)$$

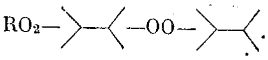
$$RO_2 + R'H \rightarrow RO_2H + R'' \xrightarrow{O_2} R'O_2^{\cdot} \qquad (5')$$

$$RO_2 + R'O_2^{\cdot} \rightarrow \text{Recombination} \qquad (6')$$

$$R'O_2^{\cdot} + R'O_2^{\cdot} \rightarrow \text{Recombination} \qquad (6")$$

From an analysis of this scheme within the framework of the method of equilibrium concentrations, it follows that the rate of formation of the oxide (I) in the presence of the second component increases if the condition $(k_2'/k_2)^2k_6/k_6" > 1$ is fulfilled. Thus, an increase in the rate of formation of olefin oxides should probably be expected after the introduction of a hydrocarbon characterized by a low recombination constant (for example, IPB) into joint oxidation with (I), so that the condition $k_6" \ll k_6$ was observed. Actually, the replacement of CB by IPB leads to an increase in the rate of formation of the oxide (I) (Fig. 3). The rates of absorption of O_2 in this case double, which is evidence of involvement of IPB in the oxidation process.

The form of the criterion of acceleration considered indicates that the rate of formation of the oxide (I) should decrease if a hydrocarbon with a relatively large recombination constant is used as the second component in the joint oxidation with (I) or (II). This confirms experiments on the joint oxidation of (I) and EB, for which $k_6" \simeq 10^7$ liters/mole·sec. As can be seen from Fig. 3, the rate of formation of the oxide (I) in the oxidation of (I) in a solvent consisting of equal volumes of EB and CB (1:1) is a little lower than in the oxidation in the absence of EB at the same rate of initiation. When CB is completely replaced by EB, the rate of formation of the oxide (I) is 1.8 times lower than in CB.

Experiments on the measurements of the chemiluminescence intensity give evidence of a change in the composition of the radicals after the addition of (I) (0.1-1 M) to a solution of EB in CB. Thus, as (I) is introduced into a solution containing 10^{-3} M AIBN, $5 \cdot 10^{-4}$ M dibromoanthracene, and 4 M EB, the chemiluminescence intensity decreases monotonically, and at a concentration ratio (EB)/(I) = 4, decreases threefold in comparison with the luminescence intensity in the absence of (I). In this case the luminescence intensity still remains several times higher than the luminescence intensity in the system AIBN—(I). Thus, chain termination occurs on peroxide radicals of (I) and the hydrocarbon R'H, just as we should have expected, in the case of joint oxidation of the two hydrocarbons [10]. The increase in the rate of formation of the oxide (I) in the presence of another hydrocarbon indicates the participation of alkylperoxide radicals of other hydrocarbons in the formation of the epoxidizing agent, which was not observed previously [16] for peroxide radicals of IPB and EB in the joint oxidation of these hydrocarbons with propylene. Evidently the rate of epoxidation depends substantially on the nature of both particles (olefin and RO_2), forming the intermediate radical 

CONCLUSIONS

1. The kinetic principles of the oxidation of the nitrile of bicyclo[2.2.1]hepten-5-oic endo(exo) acid and data on the measurement of the chemiluminescence in this process indicate that in the case of initiated oxidation of the nitrile of bicyclo[2.2.1]hepten-5-oic endo(exo) acid, there is an exchange of inhibitor radicals for olefin radicals, analogously to that observed for other hydrocarbons.

2. A scheme of oxidation of the nitrile of bicyclo[2.2.1]hepten-5-oic endo(exo) acid was proposed, which is in good agreement with the kinetic principles obtained experimentally.

3. The theoretical possibility of epoxidation of the nitrile of bicyclo[2,2,1]hepten-5-oic endo(exo) acid by peroxide radicals of isopropylbenzene and ethylbenzene in the joint oxidation of these compounds was demonstrated.

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