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R. V. KUCHER, B. I. CHERNYAK

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R. V. KUCHER, B. I. CHERNYAK

FEATURES OF THE MECHANISM OF LIQUID-PHASE OXIDATION OF BUTENE IN THE PRESENCE OF ALKALINE ADDITIVES

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There are indications in the literature that the role of alkaline additives in the liquid-phase oxidation of hydrocarbons, apart from neutralizing the acids formed in the course of the reaction, is reduced to the formation of intermediate complexes with hydroperoxide that generate free radicals (1). However, the mechanisms and the specific character of the stimulating action of alkalis in the oxidation of olefins in the liquid phase (2–5) have not yet been clarified.

In the present work, we investigated changes in the mechanism and in the ratio of the reaction products formed during the oxidation of butene in the liquid phase in the presence of sodium, calcium, and magnesium hydroxides, as well as sodium carbonate.

The oxidation of α-butene (98.5% purity), obtained by dehydration of n-butyl alcohol, was carried out in a flow-through autoclave apparatus at 120° and a pressure of 60 atm. The alkaline agents were introduced at the beginning of the reaction in the form of a finely ground powder. Peroxides were determined iodometrically, acids by titration with alkali, and the remaining products chromatographically.

The data obtained on the accumulation of individual reaction products are presented in Fig. 1. The presence in the reaction system of hydroxides of alkaline-earth metals (Mg, Ca) leads to a decrease in the rate of peroxide consumption. Along with this, in the presence of all alkaline additives, the maximum content of methylvinylcarbinol and acetaldehyde decreases. When Na_2CO_3 and NaOH are added, the total acid content is somewhat lower than in unstimulated oxidation, whereas additions of $Mg(OH)_2$ and $Ca(OH)_2$ lead to an increase in the total acid content.

It is quite interesting that in the presence of NaOH and Na_2CO_3 self-inhibition of the process sets in earlier, whereas the presence of $Mg(OH)_2$ and $Ca(OH)_2$ in the reaction system causes the reaction to proceed more deeply, with a higher degree of conversion of the olefin. In the latter case, an increase is observed in the maximum content of α-butene oxide.

The process of liquid-phase oxidation of butene is a complex chain reaction, in the elementary steps of which both radicals and intermediate reaction products take part. In our investigation of the mechanism of this process by the inhibition method it was shown that the main reaction for the formation of α-butene oxide is the reaction of interaction of the radical $RO_2\bullet$ with the double bond of the olefin, with formation of the intermediate peroxide radical $R{-}O{-}O{-}R_1\bullet$, the decomposition of which at the –O–O–bond leads to the formation of the oxide.

Addition of a system of alkaline agents to the reaction system leads to a significant decrease in the methylvinylcarbinol content, and, in the case of addition of $Mg(OH)_2$ and $Ca(OH)_2$, to an increase in the content of α-butene oxide. This fact can be explained if one takes into account the oxidative transformation of methylvinylcarbinol in the reaction mixture.

As is known, in the oxidation of secondary alcohols the primary product is peroxide compounds formed through the radical

$R(OH)O_2\cdot$ (6-9). There is no reason to doubt that the oxidation of methylvinylcarbinol also proceeds through the initial formation of peroxides. In our view, the oxidation of methylvinylcarbinol may be represented by the following general scheme.

[reaction scheme]

$$CH_2{=}CH{-}C(OH)(H){-}CH_3 \rightarrow CH_2{=}CH{-}\dot{C}(OH){-}CH_3 \xrightarrow{O_2} CH_2{=}CH{-}C(OH){-}O{-}O\cdot -$$

$$\text{path 1 (isomerization)} \rightarrow CH_3{-}C(OH){-}CH{-}CH_2O{\perp}O \rightarrow CH_3COOH + \dot{C}H_2{-}CHO \xrightarrow{+RH} CH_3CHO \rightarrow CH_3-$$

$$\text{path 2 } (+RH) \rightarrow CH_2{=}CH{-}C(OH)(OOH){-}CH_3 \xrightarrow{-H_2O_2} CH_2{=}CH{-}C(=O){-}CH_3 \rightarrow \text{a}$$

$$\text{path 3 } (+RH) \rightarrow CH_3{-}CH_2{-}CH(\dot{C}H_2){-}O{-}O{-}C(OH)(CH_3){-}CH{=}CH_2$$

$$\downarrow$$

$$CH_3{-}CH_2{-}CH{-}CH_2\ O\ + CH_2{=}CH{-}C(OH)(O\cdot){-}CH_3 \xrightarrow[-H_2O]{+RH} CH_2{=}CH{-}C(=O){-}CH_3 -$$

As follows from this scheme, the formation of α-butene oxide may occur through interaction of the radical $R(OH)O_2\cdot$ with the olefin molecule at the double bond, analogous to that given above. Naturally, in this case a larger amount of olefin should be involved in the reaction, and the carbinol content should decrease.

The proposed scheme is hypothetical in character. However, confirmation of precisely such a mechanism for the reactions in the complex process of butene oxidation is provided by the results of kinetic experiments on the oxidation of butene in the presence of methylvinylcarbinol, added to the initial hydrocarbon in an amount of 10 vol.% and 0.006 mol/l $Ca(OH)_2$. In this case, the rate of accumulation of α-butene oxide increases markedly from the very beginning of the process (Fig. 1 B, curve 7). Along with this, an increase is observed in the rate of accumulation and in the maximum concentration of methyl vinyl ketone.

Figure 1 kinetic curves

Figure 1: Figure 1 kinetic curves

The kinetic curves for accumulation of the remaining products practically do not change. Consequently, the methylvinylcarbinol present in the system is consumed via paths 2 and 3.

Table 1

Change in the concentration of hydrocarbon and α-oxide during the oxidation of α-butene in the presence of $Ca(OH)_2$, $Mg(OH)_2$ hydroxides over 6 h in comparison with unstimulated oxidation

Additive and its amount, mol/l	Increase in depth of butene conversion ΔC_b, mol/l	Increase in oxide concentration ΔC_o, mol/l	$\Delta = \Delta C_o - \Delta C_b$, mol/l	$\Delta C_o - \Delta C_b$
$Ca(OH)_2$ 0.006	0.75	0.88	0.13	1.17
$Ca(OH)_2$ 0.012	0.58	0.64	0.06	1.11
$Mg(OH)_2$ 0.0066	0.97	1.10	0.13	1.13

Taking the above into account, in the oxidation of α-butene in the presence of calcium and magnesium hydroxides, the amount of additionally formed α-butene oxide

Fig. 1. Kinetic curves for the accumulation of individual products of the liquid-phase oxidation of butene: **A**—butene consumption; —peroxides; —α-oxide; —methyl vinyl ketone; —acids; —acetaldehyde; —methyl vinyl carbinol; —crotonaldehyde without additives (1) and with additives (mol/l): NaOH 0.006 (2); Na_2CO_3 0.0057 (3); $Ca(OH)_2$ 0.006 (4); $Ca(OH)_2$ 0.012 (5); $Mg(OH)_2$ 0.0066 (6); $Ca(OH)_2$ 0.006 and 10 wt.% methyl vinyl carbinol (7) at 120° and 60 atm.

of butene must correspond to the amount of hydrocarbon additionally involved in the reaction. Comparison of these two quantities (Table 1) indeed confirms this, showing a parallelism in the change of the concentrations of the olefin and the oxide.

The somewhat higher concentration of butene α-oxide indicates the possibility of another pathway for oxide formation without additional involvement of the olefin in the reaction, for example the decomposition of the initially formed cyclic peroxides (10).

The earlier self-inhibition of the oxidation process in the presence of NaOH and Na_2CO_3 is associated with more intensive formation of inhibiting agents obtained by condensation and polymerization of the reaction products formed (carbonyl compounds, oxide, alcohol). This is confirmed by the fact that in the presence of NaOH and Na_2CO_3 the amount of carbonyl compounds in the reaction system increases, and at the same time the products of their condensation and the oxidate acquire a dark-brown color.

Table 2

Overall balance of products in the reaction system of butene oxidation in the presence of 0.006 mole/l NaOH after 4 hours in comparison with unstimulated oxidation

Component	$-\Delta C$, mole/l	$+\Delta C$, mole/l
Methylvinylcarbinol	1.13	–
Peroxides	0.096	–
Acetaldehyde	0.89	–
Acids	0.175	–
Methyl vinyl ketone	–	1.49
Crotonaldehyde	–	0.80
Total	2.291	2.29

The presence of sodium hydroxide or carbonate in the reaction system stimulates the oxidation process along pathways 1 and 2, which is confirmed by the increase in the content of methyl vinyl ketone and crotonaldehyde in the oxidate. Naturally, the decrease in the content of methylvinylcarbinol, peroxides, acetaldehyde, and acids in the reaction system must correspond to an increase in the concentration of methyl vinyl ketone and crotonaldehyde (Table 2).

The different action of sodium hydroxide and soda, on the one hand, and magnesium and calcium hydroxides, on the other, apparently consists in the formation by the latter two metals of complexes of the enol-acid type. Methylvinylcarbinol, bound in these complexes, is more readily oxidized by pathway 3. The presence of NaOH and Na_2CO_3 in the reaction system stimulates the molecular decomposition of methylvinylcarbinol hydroperoxide to methyl vinyl ketone.

Thus, the data presented confirm the idea that, during the oxidation of olefins in the liquid phase, the formation of α-oxides occurs through the interaction of radicals that carry reaction chains with the double bond of the olefin. This latter point is very important in choosing conditions for controlling the reaction in order to obtain oxides by direct oxidation of olefins.

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