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Ethylene Epoxidation under the Effect of Gas Phase Thermal Oxidation of Methane[1]

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Abstract—The process of ethylene epoxidation under the effect of gas phase thermal oxidation of methane has been studied. It was shown that if methane oxidation is carried out in the first section of two-sectional reactor and ethylene is injected into the second section then epoxidation occurs as a result of interaction of ethylene and peroxy radicals generated by methane oxidation reaction. The dependence of ethylene oxide accumulation rate on methane/oxygen ratio in the first section of reactor as well as flow velocity and temperatures in the first and second sections has been studied. The results show that in the second section of the reactor the ethylene epoxidation takes place trough $C_2H_4 + RO_2^{\bullet} \rightarrow C_2H_4O + RO$ reaction.

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Olefin oxides particularly ethylene oxide [1, 2] are the significant products of organic synthesis. Nonionic surface-active substances produced from ethylene oxide are effectively used in petroleum and petroleum-refining industries. Ethylene oxide polymerization is the way for wax-like and liquid polymers production, which are used as plasticizers and lubricants. Ethylene oxide itself [3, 4] as well as its mixtures with other compounds [5, 6] can serve as motor fuel.

At present only two methods are used for industrial production of ethylene oxide – interaction of ethylenchlorhydrin with alkaline [1] and ethylene oxidation over silver catalyst [7]. The first method is accompanied with noticeable amount of chlorine containing wastes, which pollute environment. The catalytic method of ethylene oxidation is more preferable from ecological point of view.

The most part of ethylene oxide for industrial needs is produced catalytically [8–11]. Silver and its compounds are the best catalysts of ethylene epoxidation which provide purpose compound production with selectivity exceeding 70% [12]. Nevertheless silver usage brings to several complex problems. It is known that technologies of catalyst preparation are multistage and complicated. Moreover in consequence of ageing and poisoning that take place during the exploitation, activity of catalyst is reduced so it has to be periodically regenerated. Another factor – specific requirements for initial hydrocarbon containing gases purity. The most undesirable are acetylene and sulfur compounds, which are ingredients of natural gas; the presence of other hydrocarbons as well as hydrogen and carbon oxides is unwanted to.

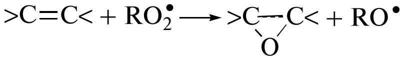
Aforesaid brings to the conclusion that working up and studies of non-catalytic gas phase processes of olefin oxides production is topical task. Gas phase process has indubitable advantages compared with catalytic one: simple apparatus, no need to use chlorine, no special requirements for initial reagents purity and elimination of expensive catalyst use.

It is known that in the course of the process of simple olefin (ethylene and propylene) gas phase oxidation alkylperoxy radicals $RO_2^{\bullet}$, which concentration exceeds 10^{14} part/cm^3 are formed [13–16]. At that, depending on process conditions (pressure and temperature) and hydrocarbon type, peroxy radicals $CH_3O_2^{\bullet}$, $C_2H_5O_2^{\bullet}$, $C_3H_7O_2^{\bullet}$, $HO_2^{\bullet}$ or their mixture can be accumulated.

Using radical freezing method combined with EPR-spectroscopy [17], authors of [18–24] have shown that at oxidation of mixtures, containing unsaturated hydrocarbons, there is a linear relationship between the rate of olefin oxide accumulation and product of peroxy radicals and olefin concentrations:

$$W = k[RO_2^{\bullet}]\,[C_2H_4]. \qquad (1)$$

Mentioned relationship indicates that epoxidation reaction takes place



$$>C{=}C< + RO_2^{\bullet} \longrightarrow >\underset{\diagdown\,O\,\diagup}{C{-}C}< + RO^{\bullet},$$

leading to olefin oxide and more active alcoxy radical formation.

Ethylene and propylene epoxidation constants, calculated on the base of experimental data can be expressed as following:

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[1] The article was translated by the authors.

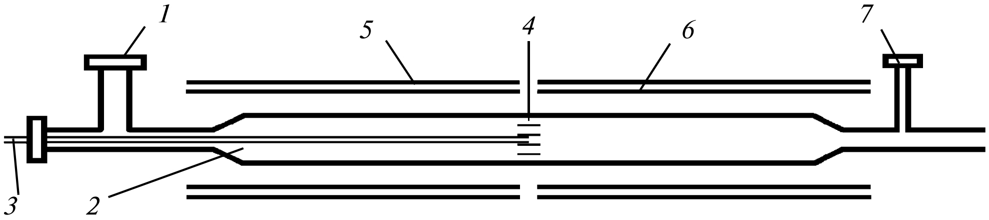

Fig. 1. Scheme of reactor: *1* – sealing device for methane-oxygen mixture feed; *2* – reactor; *3* – capillary for ethylene feed; *4* – movable packet; *5* – first section furnace; *6* – second section furnace; *7* – sealing device for sampling.

$$k_{C_2H_4O} = 0.97 \times 10^{11} \times 10^{-13760/RT}\ \mathrm{cm^3/mol\ s}$$

$$k_{C_3H_6O} = 1.86 \times 10^{11} \times 10^{-11750/RT}\ \mathrm{cm^3/mol\ s.}$$

The constant of ethylene epoxidation experimentally obtained in our study is in a good agreement with calculated value [25]. Epoxidation constants for acetylperoxy radicals $RCO_3^{\bullet}$, cited in [26, 27] are considerably higher because of their higher epoxidation ability [26–30] in comparison with alkylperoxy radicals.

As is well known, the highest concentrations of alkylperoxy radicals were detected at paraffinic hydrocarbons oxidation [31–34]. Apparently in the course of conjugated oxidation of paraffinic and olefinic hydrocarbons the favorable conditions for epoxy compounds formation can be realized. At this the main part of peroxy radicals is formed from paraffinic but not from olefinic hydrocarbon, what increases selectivity of olefin conversion into its oxide. This was confirmed by experimental data obtained at conjugated oxidation of olefinic and paraffinic hydrocarbons with equal number of carbon atoms – ethylene with ethane [35] and propylene with propane [22].

The revealed mechanism of olefin epoxidation makes it possible to define conditions essential for working up gas phase non-catalytic ways of epoxy compounds production: peroxy radicals are to be generated by means of cheap and widespread hydrocarbon containing gas oxidation; to avoid olefin consumption at the earlier stages of the process it must be fed into reaction mixture at the moment when concentration of peroxy radicals is maximal.

The purpose of present work is to realize the process of ethylene epoxidation under the effect of thermal gas phase reaction of methane oxidation.

EXPERIMENTAL

Experiments were carried out on installation which is depicted in Fig. 1. The mixture of methane and oxygen is injected trough sealing device *1* into the first section of two-sectional quartz reactor *2* (length of cylindrical part – 20 cm, diameter of reaction zone – 2 cm) where oxidation of methane occurs providing peroxy radicals formation. Ethylene is fed into the second section through capillary 3 (d = 2 mm). Movable packet *4*, consisting of quartz tubes (d = 5 mm, l = 10 mm) divides reactor for two sections. Packet movement along the reactor changes the ratio of residence times in sections. Reactor is heated using two independent electric furnaces *5* and *6*, what enables to have different temperatures in reactor sections. To perform analysis of gas phase products a sample was picked out through sealing device *7*.

To determine formaldehyde concentration, waste gases were bubbled trough distilled water for a fixed time. Bubbler was filled with fine glass breakage to increase contact surface between gas and water and, in a number of cases in order to check completeness of formaldehyde absorption, after main bubbler an additional one was placed.

Photocolorimetric analysis of obtained solution was performed using chromotropic acid. At this the concentration of formaldehyde in bubbler was determined. Formaldehyde concentration inside the reactor was calculated by formula $C = C_bVT_k/Qt_bT_r$ where C—formaldehyde concentration inside the reactor (mol/cm^3), C_b—concentration of solution from bubbler (mol/cm^3), V—water volume in bubbler (cm^3), Q—rate of gas flow through the reactor cm^3/s), t_b—duration of bubbling (s), T_k and T_r—room and reactor temperatures correspondingly (K). Partial pressure can be calculated by expression $P = P_aCN_AT_r/T_nN_L$, where P—partial pressure (kPa), T_n—normal temperature (298 K), P_a—normal pressure (101.308 kPa), N_A—Avogadro number, N_L—Loshmidt number (2.68×10^{19} part/cm^3).

Determination of gaseous products concentration was performed by means of chromatography. Methanol, ethanol, acetaldehyde and ethylene oxide were separated using chromatographic column filled with Polisorb-1 (l = 3 m, d = 3 mm, T_{col} = 378 K, Q = 30 cm^3/min, carrier gas—helium). Hydrocarbons C_1–C_4 were separated on Silipor-600 (l = 3 m, d = 3 mm, T_{col} = 363 K, Q = 24 cm^3/min, carrier gas—helium). Hydrogen, oxygen, methane and CO were separated on molecular sieves CaA (l = 2 m, d = 3 mm, T_{col} = 363 K, Q = 24 cm^3/min, carrier gas—argon). Katharometer was used as detector in all cases.

Table 1. The effect of residence times in 1-st and 2-nd sections of the reactor on yield of reaction products; $T_1 = 983$ K; $T_2 = 778$ K; $CH_4 : O_2 = 3.8$; $P = 86.7$ kPa

Mixture feed into 1 section of reactor, cm^3/s	Ethylene feed into 2 section of reactor, cm^3/s	Partial pressures of products at reactor outlet, kPa				
Q_1	Q_2	CH_3OH	CH_3CHO	C_2H_4O	HCHO	CO
1.00	0.63	0.351	0.298	0.056	0.124	3.650
1.40	0.88	0.214	0.317	1.784	0.199	3.380
1.60	1.00	0.196	0.326	2.311	0.311	2.860
1.80	1.13	0.180	0.348	2.423	0.582	2.080
2.20	1.38	0.161	0.306	1.848	0.450	1.630
2.70	1.69	0.093	0.194	1.432	0.318	0.980
3.30	2.07	0.057	0.098	0.661	0.283	0.240

Note: Q_1 and Q_2 are fixed so as to have the ratio τ_1/τ_2 the same in all experiments.

Table 2. The effect of methane/oxygen ratio in mixture injected into 1-st section of the reactor on yield of reaction products; $T_1 = 983$ K; $T_2 = 778$ K; $Q_1 = 1.80$ cm^3/s; $Q_2 = 1.13$ cm^3/s; $P = 86.7$ kP

Mixture composition inside 1 section	Partial pressures of products at reactor outlet, kPa				
$CH_4 : O_2$	CH_3OH	CH_3CHO	C_2H_4O	HCHO	CO
8.0	0.207	0.106	0.356	0.410	0.910
6.2	0.195	0.235	1.584	0.475	1.120
4.5	0.189	0.342	2.341	0.551	1.500
3.8	0.180	0.348	2.423	0.582	2.080
3.0	0.176	0.337	2.316	0.516	2.090
2.5	0.170	0.297	2.043	0.473	3.120
1.0	0.154	0.164	0.810	0.460	3.600
0.3	0.091	0.103	0.422	0.397	4.530

RESULTS AND DISCUSSION

Concentrations of main reaction products, measured for different residence times in 1-st and 2-nd sections of the reactor are given in Table 1, and those obtained for different equivalence ratio of reaction mixture injected into the first reactor section are given in Table 2. Dependences of average rate of ethylene oxide accumulation on residence time in the first section of the reactor, as well as on CH_4/O_2 ratio are shown in Figs. 2a and 2b. Calculation was performed by formula $W_{C_2H_4O} = P_{C_2H_4O}/\tau_2$, where $W_{C_2H_4O}$—average rate of ethylene oxide accumulation (kPa/s), $P_{C_2H_4O}$—partial pressure of ethylene oxide at reactor outlet (kPa), τ_2 – residence time of reaction mixture in the second section (s).

Figure 2a shows that ethylene oxide accumulation rate is maximal at residence time in the first section $\tau_1 \sim 5$ s; increase or decrease of residence time results in sharp decrease of accumulation rate. Apparently, observed relationship is conditioned by degenerate branching nature of methane oxidation, which leads to appearance of maximum on kinetic curve of peroxy radicals while residence time in the first section increases. As long as ethylene oxide accumulation rate is determined by expression (1), and ethylene concentration under conditions of Table 1 was kept the same, then the existence of maximum on the kinetic curve of peroxy radicals will cause the appearance of maximum on the dependence of $W_{C_2H_4O}$ on residence time in the first section.

As it can be seen from Table 2 and Fig. 2b the dependence of $W_{C_2H_4O}$ on $[CH_4]/[O_2]$ has a maximum – the increase of $[CH_4]/[O_2]$ from 0.3 to 3.8 leads to increase of ethylene oxide accumulation rate 5.7 times. At this change in hydrocarbon/oxygen ratio has an influence on the time of maximal concentration of peroxy radicals reach. The shape of curve in Fig. 2b can be explained by extremal dependence of hydrocarbon oxidation intensity on hydrocarbon/oxygen ratio [36]. Consequently the dependence of per-

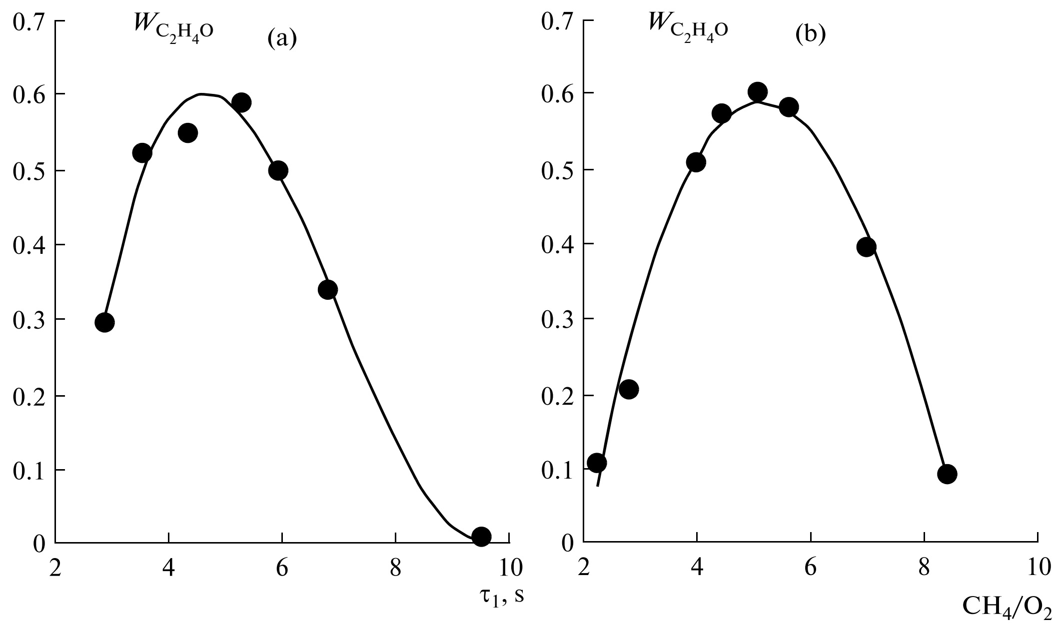

Fig. 2. Dependence of average rate of ethylene oxide accumulation on: a - residence time in the first section of the reactor at $CH_4/O_2 = 3.8$, b - ratio methane/oxygen. $Q_1 = 1.8$ cm^3/s, $Q_2 = 1.13$ cm^3/s, $T_1 = 983$ K, $T_2 = 778$ K, $P = 86.7$ kPa.

oxy radicals maximal concentration on $[CH_4]/[O_2]$ has to be a curve passed over the maximum. As a result the dependence of $W_{C_2H_4O}$ on $[CH_4]/[O_2]$ will have a maximum, what can be seen in Fig. 2b.

Under the conditions of Table 1 the experiments were carried out in which argon/oxygen mixture was injected into the first section of the reactor instead methane/oxygen; at this ethylene oxide accumulation rate was ~ 9 times lower than that in the presence of methane. Obtained result shows that ethylene epoxidation in the second section is initiated by radicals, generated in methane oxidation in 1-st section of reactor.

The influence of temperature in both sections of reactor on average ethylene oxide accumulation rate as well as concentrations of main reaction products was studied (Tables 3 and 4). It can be seen, that average ethylene oxide accumulation rate depends on temperature in the first section and passes over the maximum. Obviously it is due to degenerate branching nature of methane oxidation. At $T < 970$ K radical concentration in 1-st section does not reach its maximal value at fixed residence time and ethylene epoxi-

Table 3. The effect of temperature in 1-st section of the reactor on yield of reaction products and rate of ethylene oxide accumulation; $CH_4 : O_2 = 3.8$; $T_2 = 793$ K; $Q_1 = 1.8$ cm^3/s; $Q_2 = 1.13$ cm^3/s; $P = 86.7$ kPa

Temperature inside 1-st section, K	Partial pressures of products at reactor outlet, kPa					Rate of ethylene oxide accumulation, kPa/s
T_1	CH_3OH	CH_3CHO	C_2H_4O	HCHO	CO	$W_{C_2H_4O}$
910	0.026	0.215	0.427	0.522	1.060	0.106
927	0.032	0.296	0.664	0.521	1.130	0.165
940	0.075	0.312	1.532	0.506	1.660	0.380
965	0.114	0.334	2.193	0.502	1.760	0.544
980	0.122	0.348	2.370	0.500	1.790	0.588
993	0.132	0.360	2.439	0.493	1.900	0.605
1000	0.131	0.345	1.821	0.487	1.910	0.452
1016	0.129	0.325	0.746	0.486	1.940	0.185
1048	0.106	0.308	0.330	0.458	2.300	0.082

Table 4. The effect of temperature in 2-nd section of the reactor on yield of reaction products and rate of ethylene oxide accumulation

Temperature inside 2-nd section, K	Partial pressures of products at reactor outlet, kPa					Rate of ethylene oxide accumulation, kPa/s
T_2	CH_3OH	CH_3CHO	C_2H_4O	HCHO	CO	$W_{C_2H_4O}$
$CH_4 : O_2 = 3.8$; $T_1 = 983$ K; $Q_1 = 1.80$ cm^3/s; $Q_2 = 1.13$ cm^3/s; $P = 86.7$ kPa						
760	0.105	0.320	0.899	0.583	2.060	0.214
765	0.103	0.351	1.488	0.586	2.060	0.357
778	0.180	0.348	2.423	0.582	2.080	0.591
798	0.183	0.346	2.476	0.577	2.100	0.619
815	0.184	0.310	2.468	0.548	2.160	0.630
840	0.179	0.293	2.398	0.474	2.240	0.631
$Ar : O_2 = 3.8$; $T_1 = 983$ K; $Q_1 = 1.80$ cm^3/s; $Q_2 = 1.13$ cm^3/s; $P = 86.7$ kPa						
762	0.041	0.124	0.143	0.127	0.036	0.024
765	0.045	0.146	0.182	0.184	0.043	0.034
778	0.050	0.168	0.213	0.215	0.052	0.052
801	0.052	0.173	0.225	0.259	0.054	0.056
811	0.059	0.211	0.261	0.273	0.062	0.060
846	0.068	0.293	0.307	0.298	0.073	0.062

dation rate is lower than maximum; at $T > 1000$ K CH_4 oxidation in 1-st section is suppressed because of initial reagent consumption and concentration of radicals incoming into the second section is decreased. As a result ethylene oxide accumulation rate is decreased too, what leads to maximum appearance on the dependence of $W_{C_2H_4O}$ on temperature in 1-st section.

Data in Table 4 show that temperature increase inside the second section in the range 760–800 K increases rate of ethylene oxide accumulation almost 3 times. As conditions of methane oxidation in 1-st section remain permanent i.e. concentration of radicals incoming into the second section is the same, then rise in $W_{C_2H_4O}$ is due to increase of epoxidation constant. Further temperature increase does not noticeably change the rate of ethylene oxide accumulation, what is probably caused by ethylene oxide consumption at high (>815 K) temperatures.

With the purpose of comparison the experiments with methane substitution by argon were carried out at different temperatures as well. Obtained data (Table 4) show that in the absence of reaction in 1-st section ethylene oxide accumulation rate is decreased more than ten times. Similar conclusion was made from analysis of results obtained for different residence times.

Thus, character of dependence of ethylene oxide accumulation rate on mixture composition (in 1-st section of reactor) as well as on flow rate and temperature in both sections, is evidence of epoxidation reaction $C_2H_4 + RO_2 \rightarrow C_2H_4O + RO$ taking place (2-nd section). At that separation of epoxidizing agent (radicals $CH_3O_2^{\bullet}$, $C_2H_5O_2^{\bullet}$, $HO_2^{\bullet}$ and others) generation zone from ethylene epoxidation zone allows to reduce expensive ethylene consumption into secondary products.

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