Introduction The chemical industry is high on the list among sources of dangerous for environment. In this connection search of the new chemical processes, different low level consumption of energy and minimum formation of by-products is especially necessary. It concerns in the first place to processes of organic substances oxidation by oxygen which allows to produce a wide spectrum of products for various industries. The leader of the works devoted the creation of new high selective processes of liquid-face of oxidation by oxygen was academician N.M. Emanuel. He was sure that the main directions for increasing in selectivity of reactions of liquid-phase oxidation is the use of metal complexes as the catalysts. In the present work kinetic regularities of EG autooxidation in the presence of Cu2+-ions and the bases are investigated. As it will be shown more low, changes of conditions of carrying out of process allows to pass from highly effective oxidation EG to formic acid to reaction with primary formation of glycolic acid. It was found that at optimal conditions the rates of low temperature oxidations of EG close to rates of enzymatic reactions catalyzed by dioxygenases. Experimental Oxidation of EG by oxygen in various solvents at 30 - 90oC was spent in the glass reactor equipped with a mechanical stirrer with continues supply of oxygen. At oxygen elevated pressures (to 1 MPa) reaction was carried out in the steel reactor (volume 0.1l). In both cases stirring was carried out by means of mechanical mixers (~ 1000 rotation/min). Reactionary mixtures was preparing by consecutive introduction of salts of bivalent copper (CuCl2.2H2O, CuSO4.5H2O or Cu(Ac)2.2H2O) and alkalines (NaOH or KOH) in water or waterless solutions of EG. Alkali addition to solutions of salts of the copper, containing EG, leads to formation of brightly dark blue complexes Cu2+, stable at pH 8 ÷ 14. After addition of alkali the reactor was carefully blow of oxygen and pressurized. Oxygen absorption starts after the beginning of stirring of the reaction mix. Rate of reaction was measured on rates of oxygen absorption , an alkali and EG expenditure and accumulation of products of oxidation of EG. Acids formed in the course of reaction were analyzed by HPLC method on «Millipore Waters» with use UV detector. A column -ZORBAX SAX (4.66 x 250 mm) eluent ÷ 0.025 M solution KH2PO4. Concentration of EG was determined by GLC method [1]. Results In neutral solutions EG do not react with dioxygen with measurable rates at low 100oC . Alkaline solutions EG in the absence of copper salts do not oxidized by oxygen at low temperatures too. Thus, as well as at oxidation primary and secondary alcohols and polyols [2-5], oxidation of EG at low temperatures by oxygen is realized only in the presence of two-componential catalytic system {Cu2+ + base}. Practically at once after alkali introductions in a solution containing EG and salt of copper, intensive absorption of oxygen starts. As well as at oxidation of others hydroxy-containing compounds in the presence of copper ions and basis [6], activation of EG in relation to oxygen obviously occurs only after substrate transfer in active anionic form. The kinetic curves of oxygen absorption at the oxidation of 20 % solutions of EG in tert-butyl alcohol at 50oC in the presence of 5.10-3 M CuCl2.2H2O and various quantities [KOH] are shown on the Fig.1. Fig. 1 - Kinetic curve of oxygen absorption in reaction of

EG oxidation in the presence of various quantities of the granulated alkali. CKOH (g/l): (1) – 4 g/l; (2) – 14 g/l; (3) – 25 g/l; (4) – 50 g/l.; V = 25 ml, [CuCl2.2H2O] = 5.10-3M, PO2=0.1 MPa, [.EG]0 = 200 g/l, solvent- tert-butyl alcohol, 50oC It can be seen from Fig.1 in the range of KOH concentration 4÷25 g/l (0.07 ÷0.45M) initial rate of absorption of oxygen practically doesn't depend on concentration of alkali (Fig.1 curves 1÷3). At higher KOH concentration the rate of oxygen absorption considerably decreases (Fig. 1, curve 4) that is connected, apparently, with deactivation of the catalyst owing to formation of inactive hydroxy-complexes of bivalent copper (blue color) in the presence of the high surplus of alkali. Similar kinetic laws of oxidation EG are received at use of NaOH as basis. The maximum rates of oxidation in this case are close to rates of reaction at presence of KOH. However the small period of auto acceleration because of slower dissolution of granules NaOH in comparison with KOH in solutions was observed. During of EG oxidation in the presence of copper salts and alkali the main products are acids. After alkali neutralization by acids oxygen absorption completely stops (Fig.1 curves 1 - 3). Introduction of a new portion of alkali completely restores initial rate of oxygen absorption. The variation of total of the entered alkali allows regulate of depth of EG oxidation. Use of a method of introduction of fractional additives of alkali on a reaction course allows to spend reaction to very high depths of EG transformation (over 95%) at the highest rates of process. Rate of oxygen absorption at EG oxidation both in water and waterless solutions linearly grows with growth of Cu2+- salts concentration in the range from 0 to 2.10-2M. Further increase the copper ions concentration do not leads to change of rate of reaction. It is connected, apparently, that in these conditions (high concentration Cu2+) a limiting stage of reaction is the rate of deprotonation of EG. On Fig.2 the dependence of the rate of oxygen consumption on initial EG concentration is presented. Rise of EG concentration in a solution of tert-butyl alcohol from 0 to 50% leads to linearly increase in rate of oxygen absorption. The further increase of EG concentration, leads to considerable decrease in rate of process. It is connected, apparently, with decreasing of donor properties of anion form of EG. Earlier it was be shown [7] that aliphatic alcohols are oxidized with the highest rates only in aprotic solvents. Similar influence of the nature of solvent used on the rate of EG oxidation is observed too. Fig. 2 - Dependence of the rate of EG oxidation from its concentration (vol. %) in a solution of tert-butanol. [CuCl2.2H2O] = 5.10-3M, [KOH]o = 0.5M, PO2 =0.1MPa, solvent tert-butanol, 50oC As it is possible to see from Fig.3 the highest rates of oxygen combustion in reaction of EG oxidation are reached if the most polar aprotic solvents, such as DMSO (column 1) and DMF (column 2) are used. At the use of H-containing solvents rate of reaction are decreasing and in water containing solvent (column 8) makes not more than 2-3% from the value of rate of EG oxidation in DMSO. Fig. 3 - Rates of oxygen absorption (WO2 ,white bar) and selectivity of formic acid formation (S, grey bar) □ at EG oxidation in various solvents: 1 – DMSO, 2 – DMF, 3 – ethanol, 4 – EG, 5 – diglym, 6- tert-butanol, 7 – 2-propanol, 8 – water; [CuCl2.2H2O] = 5.10-3M,

[KOH]o= 0.5 M, 50oC, [EG] = 20% vol. (1-3; 5-8), [EG] = 100 % vol. (4). PO2 =0.1 MPa The analysis of products of EG oxidation by GLC and HPLC methods has shown that in the course of reactions in all investigated conditions as the basic products of reaction acids are formed. Depending on conditions of carrying out of process EG can be oxidized to formic acid (with selectivity close to 100%) or with primary formation glycolic acids. At optimum conditions (not water containing solutions and low temperatures) salts of formic acid are the unique products of EG oxidation (reaction I): HOCH2-CH2OH + 1.5O2 + 2KOH → 2HCOOK + 3H2O (1) On Fig.3 along with the rates of absorption of oxygen data, the data on selectivity of formation of formic acid on EG concentration is presented. The greatest selectivity of formation of formic acid, coming nearer to 100%, is observed in case of oxidation pure EG (column 4) and 25% of solutions in tert-butyl alcohol (column 6). Oxidation of water solutions of EG leads to sharp decrease in rate of reaction. In the presence of water, unlike oxidation EG in waterless environments, the basic product of oxidation EG is not formic but glycolic acid (reaction 2). HOCH2-CH2OH + O2 + KOH→HOCH2-COOK+2H2O (2) In Table 1 the date on rate of oxygen absorption and selectivity of formic and glycolic acids formation is presented. Increase in concentration of water above 10% in mix of H2O – tert-butyl alcohol leads to sharp decrease in rate of absorption of oxygen and to considerable increase of concentration glycolic acids in products of EG oxidation. Table 1 - Rates of O2 absorption (WO2) and selectivity of formic (SHCOOH, %) and glycolic (SHOCH2COOH, %) acids formation in solution H2O – tert-butanol at various concentrations of H2O in a mix (vol. %).[CuCl2.2H2O]o=5.10-3M, [EG] =20% vol., [KOH]0 =0.5M, T=50oC, PO2 =0.1MPa Contents of H2O in the mix H2O – tert-butanol, vol % 0 5 10 25 50 100 WO2.105,M/s 6.8 6.6 5.9 2.5 1.1 0.5 SHCOOH, % 96 93 91 77 45 40 SHOCH2COOH, % 1 5 7 19 40 52 In Table 2 the rates of oxygen absorption data at various temperatures are presented. Table 2 - Rates of O2 absorption and selectivity of formation formic and glycolic acids at various temperatures. [CuCl2.2H2O]o=5.10-3M, [EG] =20% vol., [KOH] =0.5M, PO2=0.1 MPa., solvent – tert-butanol Temperature,oC 30 40 50 60 70 80 W O2.104, M/s 0.1 0.33 0.68 1.05 1.7 1.71 SHCOOH, % 98 97 96 91 80 55 SHOCH2COOH% 0 0.5 1 4 5 12 In the range of temperatures from 30 to 70oC classical Arrhenius dependence is observed: energy activation is 43 kJ/mol. However at rise in temperature above 70oC rate of absorption of oxygen doesn't increase. It is possible to see that at rise in temperature from 70 to 80oC in reaction of oxidation of 20% vol. solution of EG in tert-butyl alcohol selectivity of formic acid formation decrease from 80 to 55%. It is connected, apparently, with the rise of a rate oxidation of K-salts of EG to CO2 Oxidation of EG in a bulk at two temperatures - 50 and 90oC was studied too (Table 3). Table 3 - Rates and selectivity of formic and glycolic acids formation at 50oC and 90oC. [CuCl2.2H2O] = 5.10-3M, [KOH]0 = 0.4M, PO2 =0.1MPa.100% vol. EG. T oC WO2.104 M.s-1 SHCOOH, % SHOCH2COOH, % 50 1.0 95.0 3.5 90 0.9 35.0 55.0 As can be seen from this table, rise in temperature on 40oC leads to decrease in rate of oxygen absorption and to change of a direction of process. If at low temperatures almost unique product of oxidation is formic acid, at 90oC EG is oxidized mainly to glycolic acids. Dependence of rate of oxidation EG from partial pressure of oxygen is unusual to reactions of liquid phase oxidations of organic connections. In Table 4 the data of influence on rate and selectivity of EG oxidation to formic acid in tert-butyl alcohol from O2 pressure are presented. Selectivity of formic acid formation was determent as the relation of concentrations of HCOOH formed to concentration of hydroxide potassium spent. It is well known that the rate of liquid phase oxidations of organic substrates in the presence of initiators or traditional catalytic systems in neutral environments practically do not depend from partial pressure of oxygen at PO2 from above 0.02 MPa [8] Table 4 - Rates and selectivity of formic acid formation at various pressure of oxygen. Solvent tert-butanol, EG 25% vol, [CuCl2.2H2O] = 5.10-3M, [KOH]0 = 0.5M, 50oC Partial presser of O2 Rate of KOH consumption M.s-1 Selectivity of HCOOH formation, % 0.02 MPa. 2.1.10-5 45 0.1 MPa. 6.3.10-5 90 1.0 MPa. 3.2.10-4 » 100 As it is possible to see from Table 4 considerable growth of rate of oxidation EG is observed at least up to values PO2 – 1MPa. At the low pressure of oxygen (0.02 MPa.) not only low rate of oxidation of EG is observed, but low selectivity of formic acid formation too. At elevated pressures of O2 and at low temperatures the unique product of reaction is HCOOH. Discussion of results The kinetic regularities of EG oxidation by O2 resulted in an experimental part demonstrate that in the presence of ions of bivalent copper and alkali reaction proceeds via the uncommon mechanism. Extraordinary strong dependence of the rate and the direction of EG oxidation on the nature of solvent used was found. Dependence of rate and selectivity of oxidation on temperature is uncommon too. Besides that dependence on rate of reaction from partial pressure of oxygen is atypical for reactions of liquid phase oxidations of organic substrates by oxygen. On the basis of the received experimental data it is possible to draw a conclusion that in most cases (waterless environments, moderate temperatures) oxidation proceeds through the stage of chelate complexes formation between Cu2+-ions and dianionic forms of EG. Dark blue complexes of bivalent copper with dianionic form of EG are formed practically immediately after alkali additions to solution containing of EG and Cu2+salts. Such complexes possess very high stability. They have been allocated from solutions and characterized by a method X-ray analysis [9]. It is known that bivalent copper ions can catalyze oxidation by molecular oxygen of some easily oxidized compounds such as phenols, pyrocatechol, etc. which are in anionic form. In such reactions, as it has been shown [10], bivalent copper ions act as oxidants and the role of oxygen consists in reoxidation of unstable Cu+ cations, formed on the first stage of reaction, to Cu2+ ions. Differ of this, Cu2+ complexes with dianionic form of EG in the absence of oxygen are stable, that can be confirmed by spectral analysis of such complexes. Thus, the mechanism of the reaction which suppose the stage of EG ions oxidation by bivalent copper ions (reaction 3) must be excluded from consideration: Cu2+ … - OCH2CH2O - s //® Cu+ ….OCH2CH2O - (3) It was possible to assume that as active intermediates in reaction of EG oxidation are the reduced forms of oxygen, such as superoxide-anion radical or hydrogen peroxide. It is well known, that superoxide-anion radicals are absolutely unstable at presence even water traces. But, as it is possible to see from Table 1, introduction in a solution from 5 to 10% vol. water practically doesn't influence on rate of oxygen consumption. . On Fig.4 the kinetic curve of oxygen absorption in the reaction of EG oxidation in tert-butyl alcohol at introduction in a reactionary mix of additives of 30% of solution H2O2 is presented. One can see that after introductions of H2O2 in solution an intensive allocation of oxygen is observed . During 3 ë5 minutes almost all entered hydrogen peroxide decompose on oxygen and H2O. The products of EG oxidation are almost similar to that as in without H2O2 addition. Fig. 4 - The kinetic curve of oxygen consumption in reaction of EG oxidation (20% vol.) in tert-butyl alcohol. Arrows specify the moment of introduction in the reactionary mix of 30% of solution H2O2 in quantity: (1) – 1.9 mmol, (2) – 3.8 mmol H2O2; V= 25 ml, [CuCl2.2H2O] = 5.10-3 M, [KOH]o = 0.3M, 50oC, PO2 =0.1 MPa As it was specified above, numerous reactions of primary and secondary alcohols, glycols, ketones in the presence of complexes of copper and the bases proceeds, apparently, via thermodynamic favorable multi electronic mechanism of carrying over electrons from anionic forms of substrates, coordinated on Cu2+ the centers, on O2 molecules [1-7]. Efficiency of direct interaction of coordinated anions with O2 is in many respects defined their donor by ability. The results on influence of rates of EG oxidation by nature solvent confirm this. The highest rates of oxidation are observed when the process carrying out in DMSO or DMF (Fig.3), i.e. when the solvents in which donating ability anions the highest are used [11]. At process carrying out in the water, owning the most strong proton donating ability, exceptional drop in a rate of reaction is observed. High stability of complexes of copper with anionic form of EG to redox transformations in the absence of oxygen and unusually strong dependence of rate of reaction to partial pressure of oxygen, confirm that direct attack O2 to a complex of bivalent copper with anionic form of EG is limiting stage of reaction. The received kinetic dates of oxidation of EG allow to assume that formation of formic acid results from interaction O2 with chelate complexes {Cu2+ … A2-} (where A2- dianionic form of EG). Stability of such complexes in alkaline solutions, as it was already marked, very high. Increase of concentration of anions Cu2+ leads to increase of concentration of such complexes and linear increase of rate of oxygen consumption of and the rate of formic acid formation. The structure of copper complexes with dianionic form of EG in very strong degree depends of temperature and nature of solvent used. It is known, that stability of chelate complexes of transition metals decreases at rise in temperature. Replacement aprotic solvents on water also should lead to decomposition of copper complexes with EG-dianions due to water, as known, is the most powerful hydrolyzing agent. On the basis of the represented experimental data it is possible to assume that the first stage of the reaction leading to formation of formic acid is the interaction of {Cu2+ … A2-}

complex with O2, where A2- - dianionic form of EG. Abnormal strong dependence of rate of reaction on partial pressure of oxygen conforms this supposition. It was noticed that complexes Cu2+ with anionic form of EG are very stable in anaerobic conditions (reduction of Cu2+ ions to Cu+ do not proceed with measurable rates). It is can be assume that formic acid is the product of subsequent oxidation of primary product - glycolic acid. But introduction glycolic acid in a EG solution (in the presence of 5.10-3 CuCl2.2H2O, 0.2 M of glycolic acids and 0.5M KOH in tert-butyl alcohol, 50oC) do not change the rate of process and rate of formic acid accumulation. It is not conformed with the assumption of participation glycolic acids as intermediate in HCOOH formation. Oxidizing rupture of C-C bonds in EG molecule can leads to methanol or formaldehyde formation, also possible intermediates in formic acid formation. However, methanol even as traces was not detected in products of EG oxidation. Earlier it was shown, that formaldehyde which could be formed as intermediate compound, in alkaline environments in the presence of copper ions is oxidized with high rates, but with very low selectivity of formic acid formation [12]. Reaction of EG oxidation to formic acid proceed, apparently, via the concert mechanism and includes multi-electronic reduction of oxygen without formation stable intermediates. It is known, that such processes with participation O2 as an oxidizer is most favorable from the thermodynamic point of view [13]. The participation Cu2+ ions in the process of electrons transfer from coordinated anion form of substrate to O2 molecule open possibility of reaction proceeding by concert multi-electron mechanism without formation of free radicals. Proceeding of process by thermodynamically advantage multi-electron mechanism of oxygen reduction allows reach of extremely high rates of oxidation at room temperatures at selectivity of formation of final products exceeding 90%. Conclusions The resulted experimental data show that at use of oxygen as the cheapest and non-polluting oxidizer and simple catalytic system [Cu2+ … substrate … OH-] is possible to oxidize with extraordinary rates even such inert in relation to O2 organic compounds as EG. It was shown, that varying conditions of carrying out of process it is possible to obtain as a main product glycolic or formic acid with high selectivity. The rates of processes are near to that of enzymatic reactions at the presence of dioxygenases.