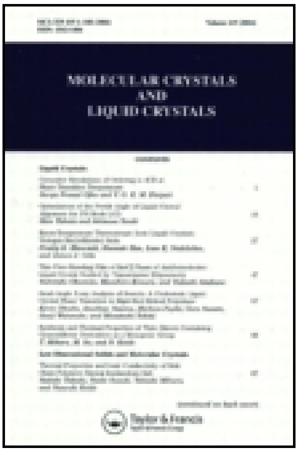

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Catalytic Oxidation of Ethylene Glycol by Dioxygen in Alkaline Medium. The New Example of One-Stage Oxidative Cleavage of C—C Bond

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Reaction of low temperature oxidations of ethylene glycol (EG) by molecular oxygen in the presence of salts of bivalent copper and alkali both in water and in waterless solutions was investigated. It was found that at low (close to room) temperatures for the process carrying out in waterless solutions the basic product of EG oxidation is formic acid. Rising the temperature from 290–315 K to 350–360 K or carrying out the reaction in water-containing solutions leads to sharp change of a direction of reaction. EG in these conditions is oxidized with primary formation of glycolic acids salts. The change of direction of reaction is connected, apparently, with decrease stability of chelate complexes of Cu^{2+}*-ions with dianionic form of EG. The mechanism of glycolic acids formation includes, possibly, a stage of two-electronic reduction of* O_2 *in reaction of dioxygen with monoanionic forms of EG, coordinated on* Cu^{2+}*-centers.*

Keywords Cu^{2+}-ions catalysis; ethylene glycol; formic and glycolic acids formations; oxidation by oxygen

Introduction

The search on new chemical processes, different low level consumption of energy and minimum formation of by-products are 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 to creation of new high selective processes of liquid-face of oxidation by oxygen was academician N. M. Emanuel [1]. He was sure that the main direction 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 Cu^{2+}-ions and bases are investigated. As it will be shown later, changes of conditions of carrying out the 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 are close to rates of enzymatic reactions catalyzed by dioxygenases.

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Experimental

Oxidation of EG by oxygen in various solvents at 300–360 K was carried out in a glass reactor equipped with a mechanical stirrer with continues supply of oxygen. At oxygen elevated pressures (up to 1 MPa) reaction was carried out in the steel reactor (volume 0.1 L). In both cases stirring was carried out by means of mechanical mixers ($\sim$1000 rotation/min).

Reactionary mixtures was prepared by consecutive introduction of salts of bivalent copper ($CuCl_2.2H_2O$, $CuSO_4.5H_2O$ or $Cu(Ac)_2.2H_2O$) 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 Cu^{2+}, stable at pH $8 \div 14$. 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.

The 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 during the reaction were analyzed by HPLC method on «Millipore Waters» with UV detector. A column-ZORBAX SAX (4.66 × 250 mm) and as eluent $\div$ 0.025 M solution KH_2PO_4 were used. Concentration of EG was determined by GLC method [2].

Results

In neutral solutions EG do not react with dioxygen with measurable rates at temperature lower 373 K. Alkaline solutions EG in the absence of copper salts do not oxidized by oxygen at low temperatures too. Thus, similarly as oxidation of the primary and secondary alcohols and polyols [3–6], oxidation of EG at low temperatures by oxygen is realized only in the presence of two-componential catalytic system $\{Cu^{2+} + \text{base}\}$.

Practically immediately after alkali introductions in a solution containing EG and salt of copper, intensive absorption of oxygen starts. Similarly as oxidation of others hydroxy-containing compounds in the presence of copper ions and basis [7], the reaction of EG with oxygen obviously occurs only after the substrate is transformed in an active anionic form.

The curves of oxygen absorption for the oxidation of 20% solutions of EG in tert-butyl alcohol at 323 K in the presence of 5.10^{-3} M $CuCl_2.2H_2O$ and various quantities [KOH] are shown in Fig. 1.

It can be seen from Fig. 1 that in the range of KOH concentration $4 \div 25$ g/L ($0.07 \div 0.45$ M) initial rate of oxygen absorption practically does not depend on concentration of alkali (Fig. 1 curves $1 \div 3$). 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 obtained when NaOH was used as basis. The maximum rates of oxidation in this case are close to rates of reaction obtained in presence of KOH. However the small period of auto acceleration because of slower dissolution of NaOH granules 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 the total entered alkali allows to control the EG oxidation. Using a method of introduction of fractional quantities of alkali during the reaction allows

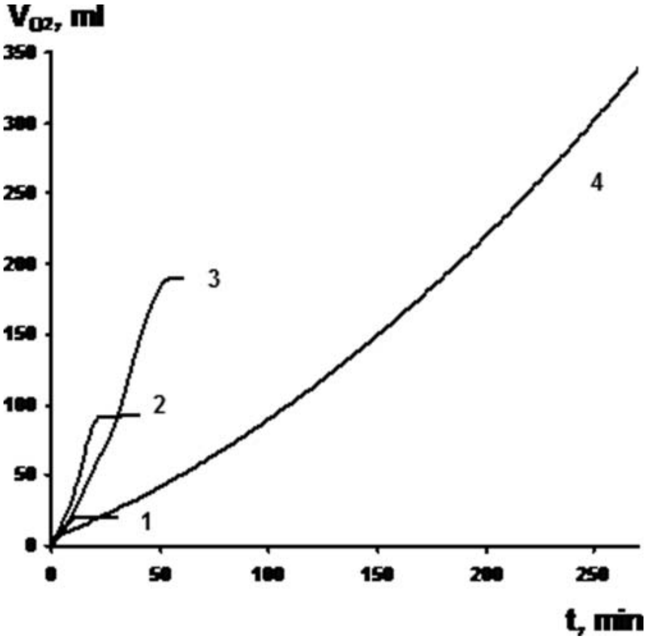

Figure 1. Curves of oxygen absorption in reaction of EG oxidation in the presence of various quantities of the granulated alkali. C_{KOH}: (1) – 4 g/L; (2) – 14 g/L; (3) – 25 g/L; (4) – 50 g/L.

to conduct the reaction to very high yields 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 Cu^{2+}-salts concentration increase in the range 0 to 2.10^{-2} M. Increasing the copper ions concentration above 2.10^{-2} M do not leads to change of rate of reaction. It is due to the fact that at high concentration Cu^{2+} the limiting stage of reaction is the rate of deprotonation of EG.

In Fig. 2 the dependence of the rate of oxygen consumption on initial EG concentration is presented. Rising the EG concentration in a solution of tert-butyl alcohol from 0 to 50% leads to linearly increase of the rate of oxygen absorption. Higher EG concentration leads to considerable decrease in rate of process. This is due to the decreasing of donor properties of anion form of EG. It was shown [8] 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.

As it can be seen from Fig. 3 the highest rates of oxygen absorption in reaction of EG oxidation are reached if the most polar aprotic solvents, such as DMSO (column 1) and DMF (column 2) are used. When H-containing solvents were used, the rate of reaction is dramatic decreasing being less than 2–3% from the value of rate of EG oxidation in DMSO for water containing solvent (column 8).

The analysis of products of EG oxidation by GLC and HPLC methods has shown that during the reaction in all investigated conditions as the basic products of reaction acids are formed. Depending on conditions of carrying out the process EG can be oxidized to formic acid (with selectivity close to 100%) or with primary formation glycolic acids.

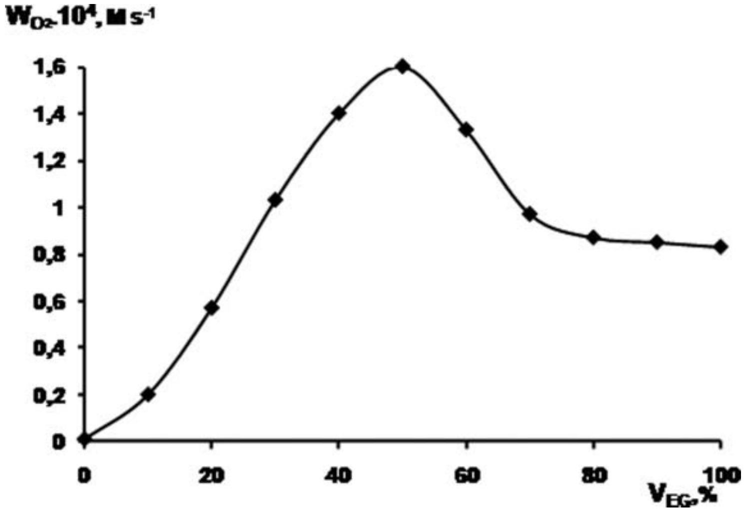

Figure 2. Dependence of the rate of EG oxidation on initial EG concentration (vol. %) in a solution of tert-butanol.

At optimum conditions (not water containing solutions and low temperatures) salts of formic acid are the unique products of EG oxidation (reaction 1):

$$HOCH_2\text{-}CH_2OH + 1.5O_2 + 2KOH \rightarrow 2HCOOK + 3H_2O \qquad (1)$$

In Fig. 3 data on selectivity of formation of formic acid on EG concentration are presented too. The greatest selectivity of formation of formic acid, almost 100%, is observed in case of pure EG oxidation (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 salts of formic but salts of glycolic acid. (reaction 2). Potassium salt

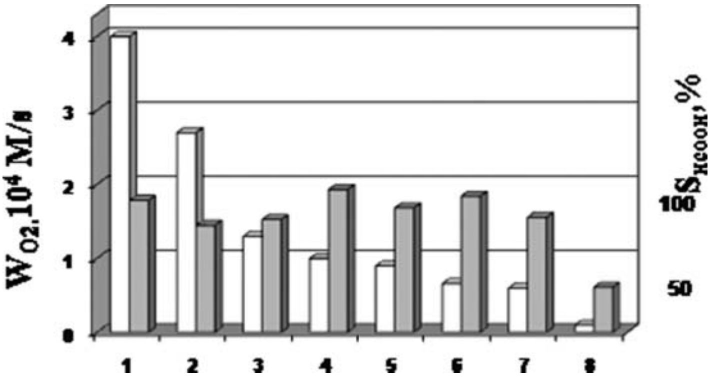

Figure 3. Rates of oxygen absorption (W_{O_2},white bar) and selectivity of formic acid formation (S, grey bar) at EG oxidation in various solvents: 1 – DMSO, 2 – DMF, 3 – ethanol, 4 – EG, 5 – diglym, 6 – tert-butanol, 7 – isopropanol, 8 – water.

Table 1. Rates of O_2 absorption (W_{O_2}) and selectivity of formic (S_{HCOOH}, %) and glycolic (S_{HOCH_2COOH}, %) acids formation in solution H_2O—tert-butanol at various concentrations of H_2O in a mix (vol. %)

Contents of H_2O in the mixture H_2O—tert-butanol, vol %	0	5	10	25	50	100
$W_{O_2}.10^5$, M/s	6.8	6.6	5.9	2.5	1.1	0.5
S_{HCOOH}, %	96	93	91	77	45	40
S_{HOCH_2COOH}, %	1	5	7	19	40	52

of glycolic acid at low temperatures in the presence of alkali and Cu^{2+} salts is stable.

$$HOCH_2\text{-}CH_2OH + O_2 + KOH \rightarrow HOCH_2COOK + 2H_2O \qquad (2)$$

In Table 1 data on rate of oxygen absorption and selectivity of formic and glycolic acids formation are presented. Increasing water concentration above 10% in the mixture H_2O—tert-butyl alcohol leads to sharp decrease of the rate of absorption of oxygen and to considerable increase of glycolic acids concentration.

In Table 2 the rates of oxygen absorption data at various temperatures are presented. In the range of temperatures from 300 to 340 K classical Arrhenius dependence is observed: energy activation is 43 kJ/mol. However increasing the temperature above 343 K the absorption rate of oxygen doesn't increase. It is possible to see that increasing the temperature from 340 to 350 K in reaction of oxidation of 20% vol. solution of EG in tert-butyl alcohol selectivity of formic acid formation decrease from 80 to 55%. This is due to the rise of the oxidation rate of K-salts of EG to CO_2.

Oxidation of EG in a bulk at two temperatures—323 and 363 K was studied too (Table 3).

As can be seen from Table 3, increasing the temperature to 363 K 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 363 K 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 O_2 pressure are presented.

Selectivity of formic acid formation was determined as the relation of concentrations of HCOOH formed to concentration of hydroxide potassium reacted. It is well known that the rate of liquid phase oxidations of organic substrates in the presence of initiators or

Table 2. Rates of O_2 absorption and selectivity of formation formic and glycolic acids at various temperatures

Temperature K	303	313	323	333	343	353
$W_{O_2}.10^4$, M/s	0.1	0.33	0.68	1.05	1.7	1.71
S_{HCOOH}, %	98	97	96	91	80	55
S_{HOCH_2COOH}, %	0	0.5	1	4	5	12

Table 3. Rates and selectivity of formic and glycolic acids formation at 323 and 363 K in bulk EG oxidation

T, K	$W_{O_2}.10^4$ M.s^{-1}	S_{HCOOH}, %	S_{HOCH_2COOH}, %
323	1.0	95.0	3.5
363	0.9	35.0	55.0

traditional catalytic systems in neutral environments practically do not depend on partial pressure of oxygen for pO_2 above 0.02 MPa [1]. As it is possible to see from Table 4 considerable growth of rate of oxidation EG is observed for pO_2 of 1 MPa. At 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 high O_2 pressures and low temperatures the unique product of reaction is HCOOH.

Discussion of Results

The kinetic regularities of EG oxidation by O_2 showed in the experimental part demonstrate that in the presence of ions of bivalent copper and alkali the reaction proceeds via an 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. Moreover the dependence of rate of reaction on 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 Cu^{2+}-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 Cu^{2+} salts. Such complexes possess very high stability. They have been removed from solutions and characterized by X-ray analysis [9].

It is known that bivalent copper ions can catalyze the oxidation by molecular oxygen of some easily oxidized compounds such as phenols, pyrocatechol, etc. which are in anionic form. In such reactions, bivalent copper ions act as oxidants and the role of oxygen consists in reoxidation of unstable Cu^+ kations, formed on the first stage of reaction, to Cu^{2+} ions [10]. Contrary of this, Cu^{2+} 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

Table 4. Rates and selectivity of formic acid formation at various oxygen pressure

Partial pressure of O_2	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

copper ions (reaction 3) must be excluded from consideration:

$$\mathrm{Cu}^{2+}\cdots{}^{-}\mathrm{OCH_2CH_2O^-} -//\rightarrow \mathrm{Cu}^{+}\cdots{}^{\cdot}\mathrm{OCH_2CH_2O^-} \quad (3)$$

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 in the presence of even water traces. But, as it is possible to see from Table 1, introduction in a solution of 5 to 10% vol. water practically does not influence the oxygen rate consumption.

In Fig. 4 the curve of oxygen absorption for the reaction of EG oxidation in tert-butyl alcohol when 30% H_2O_2 was added in the reaction mixture is presented. One can see that after introductions of H_2O_2 in solution the oxygen consumption is strongly perturbed. During $3 \div 5$ minutes almost all entered hydrogen peroxide decompose on oxygen and H_2O. The products of EG oxidation are almost similar to that obtained without H_2O_2 addition.

As it was specified above, numerous reactions of primary and secondary alcohols, glycols, ketones in the presence of copper complexes and the bases proceeds, apparently, via thermodynamic favorable multi electronic mechanism of carrying over electrons from anionic forms of substrates, coordinated on Cu^{2+} centers, on O_2 molecules [2–8]. The rate of interaction of coordinated anions with O_2 is in many respects depending on their donor ability. The results on influence of rates of EG oxidation by nature of 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 are the highest used [11]. For the process carrying out in water, owned by the strongest proton donating ability, exceptional drop in the 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

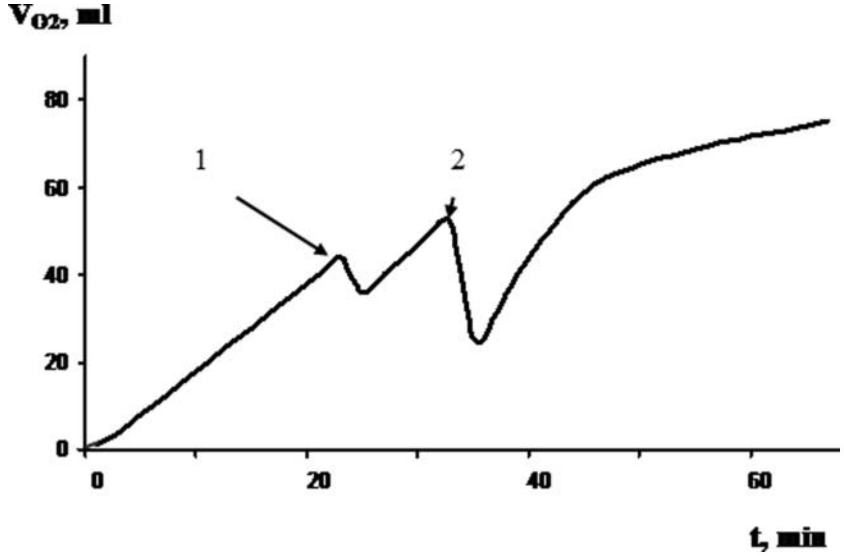

Figure 4. The curve of oxygen consumption in reaction of EG oxidation (20% vol.) in tert-butyl alcohol. Arrows specify the moment of introduction in the reaction mixture of 30% of solution H_2O_2 in quantity: (1) – 1.9 mmol, (2) – 3.8 mmol H_2O_2.

pressure of oxygen, confirm that direct attack of O_2 to a complex of bivalent copper with anionic form of EG is the limiting stage of reaction.

The obtained kinetic data of oxidation of EG allow to assume that formation of formic acid results from interaction O_2 with chelate complexes $\{Cu^{2+} \cdots A^{2-}\}$ (where A^{2-} dianionic form of EG). Stability of such complexes in alkaline solutions, as it was already marked, is very high. Increasing the concentration of anions Cu^{2+} leads to increase of concentration of such complexes and linear increase of rate of oxygen consumption and of formic acid formation.

The structure of copper complexes with dianionic form of EG strongly depends on temperature and nature of solvent used. It is known, that stability of chelate complexes of transition metals decreases when temperature increase. Replacement of aprotic solvents with water also should lead to decomposition of copper complexes with EG-dianions due to water, which, is the most powerful hydrolyzing agent.

Based on 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 $\{Cu^{2+} \cdots A^{2-}\}$ complex with $O_{2,}$ where A^{2-} - dianionic form of EG. Abnormal strong dependence of rate of reaction on partial pressure of oxygen conforms this supposition. It was noticed that complexes Cu^{2+} with anionic form of EG are very stable in anaerobic conditions (reduction of Cu^{2+} ions to Cu^{+} do not proceed with measurable rates).

It can be assumed that formic acid is the product of subsequent oxidation of primary product—glycolic acid. But introduction of glycolic acid in a EG solution (in the presence of 5.10^{-3} $CuCl_2.2H_2O$, 0.2 M of glycolic acids and 0.5 M KOH in tert-butyl alcohol, 323 K) do not change the rate of process and rate of formic acid accumulation. It is not conformed to the assumption of participation of 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 multi-electronic reduction of oxygen without formation of stable intermediates. It is known, that such processes with participation of O_2 as an oxidizer is most favorable from the thermodynamic point of view [13]. The participation Cu^{2+} ions in the process of electrons transfer from coordinated anion form of substrate to O_2 molecule open the possibility of reaction proceeding by multi-electron mechanism without formation of free radicals. Proceeding the process by thermodynamically advantage multi-electron mechanism of oxygen reduction allows to reach extremely high rates of oxidation at room temperatures with a selectivity of formation of final products exceeding 90%.

Conclusions

The obtained experimental data show that at use of oxygen as the cheapest and non-polluting oxidizer and simple catalytic system $[Cu^{2+} \cdots \text{substrate} \cdots OH^{-}]$ is possible to oxidize with extraordinary rates even such inert in relation to O_2 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 in the presence of dioxygenases.

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