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REACTIONS OF OZONE WITH ALCOHOLS, KETONES, ETHERS AND HYDROXYBENZENES (PART 1)

Keywords: ozonation, alcohols, ketones, ethers, hydroxybenzenes, kinetics, mechanisms.

The paper is focused on degradation of organics by ozonation and it comprises various classes of oxygen-containing organic compounds – alcohols, ketones, ethers and hydroxybenzenes. The mechanisms of ozone reactions with these compounds in organic solvents are discussed in details, the reaction schemes and the corresponding kinetic and some thermodynamic parameters are given. The dependences of the kinetics and the mechanism of the ozonation reactions on the structure of the compounds, on the medium and on the reaction conditions are revealed. The various possible applications of ozonolysis are specified and discussed. All these reactions have practical importance for the protection of the environment.

Ключевые слова: озонирование, спирты, кетоны, эфиры, гидроксибензены, кинетика, механизмы.

В статье рассматривается разложение органических веществ путем озонирования различных классов кислородсодержащих органических соединений – спиртов, кетонов, эфиров и гидроксибензенов. Обсуждены механизмы реакций озона с этими соединениями в органических растворителях, представлены соответствующие схемы реакций и приведены соответствующие кинетические и некоторые термодинамические параметры. Выявлены зависимости кинетики и механизма реакций озонирования от структуры соединений, среды и условий проведения реакций. Указаны и обсуждены различные возможности применения озонолиза. Все эти реакции имеют практическое значение для защиты окружающей среды.

Introduction

The ozonolysis of oxygen-containing compounds is a promising process that takes place under mild conditions and yields compounds of a higher oxidation state than that of the starting compounds. It may find various applications in chemical and pharmaceuticals industries, fine organic synthesis, etc. (1-2). The widest application, in this respect, has been found for the oxidation of primary and secondary alcohols respectively into their corresponding aldehydes and ketones. For example in the cases of the oxidation of open-chain (simple) and cyclic secondary alcohols the yield of ketones is within the range 57% up to 83% (3). Moreover, the considered interactions are extremely important from an ecological point of view for the utilization and purification of industrial wastewaters, originating from hydroxybenzene production, through their partial or complete oxidation (4-24). The importance of this process for theory and practice gave us an impetus to carry out systematic investigations (25-35). The aim of the present paper is the precise determination of the rate constants of ozonolysis of some more widely occurring representatives of the studied classes of organic compounds. Applying the activated complex method (ACT) (36) and collision theory (CT) (36) some theoretical investigations have also been carried out elucidating the structure of the transition state formed in the course of the reaction. On the basis of the correlation between the results from the experimental and theoretical studies some peculiarities in the mechanism of ozone reactions with the considered classes of oxygen containing compounds have been established.

Experimental

Ozone has been obtained from dry oxygen by means of a silent discharge of 5-8 kV at an oxygen flow rate of 0.1 L/min. The ozone concentration, 10^{-5}-10^{-3} M, has been measured spectrophotometrically in the wavelength region of 254-300 nm in a 5 cm quartz gas cell.

Methods

The UV, IR, ESR spectra were registered on standard equipments, as well as HPLC, and GC analyses.

Kinetic Measurements

Static Method

Pure reagent or reagent solution was injected into thermostatic 1 cm quartz cuvette, containing a solution of ozone in CCl_4, the time of mixing being less than 0.2 second. Ozone concentration was monitored spectrophotometrically in the region of 270-290 nm. At $[RH]_o/[O_3]_{lo}>100$, the ozone pseudomonomolecular constant $k`=k[RH]_o$ was determined on the basis of the equation $lg([O_3]_{lo}/[O_3]_{lt})=k`t$ where $[O_3]_{lo}$ and $[O_3]_{lt}$ are the initial and current concentrations of ozone in solution, respectively (27).

Dynamic Method

The ozone was bubbled through a cylindrical glass reactor with inner diameter ∅=1.7-3.7 cm and height 7-15 cm, supplied with porous glass grit-G2 at its bottom. The accuracy of maintaining constant temperature was ±0.1°C. Conventionally, gas flow rate was v=0.1 L/min; the solutions volume was V=10 ml; the ozone concentrations at the reactor inlet ($[O_3]_o$) varied from 10^{-6} to 10^{-3} M; the solvent was CCl_4; $[RH]_o=10^{-4}$-10^{1} M. The inlet and outlet ozone concentrations were measured in the gas phase in the 254-300 nm wavelength range. The determination of rate constants is based on the approach, which connects the balance of consumed ozone with the rate of the chemical reaction - Eq. (1):

$$\omega([O_3]_o-[O_3]_g) = k[O_3]_l[RH] \qquad (1)$$

where ω is the relative flow rate of ozone–oxygen gas mixture (in litres per L of solution per sec); $[O_3]_o$ and

$[O_3]_g$ are the ozone concentrations at the reactor inlet and outlet, respectively, $[O_3]_l$ is ozone concentration in the solution; $[RH]$ is concentration of the reagent. This model is valid in all cases, when the rate of ozone absorption is considerably greater than the rate of the chemical reactions. If in the case of a bimolecular reaction, in accordance with Henry's Law, $[O_3]_l$ is substituted with $\alpha[O_3]_g$, where α is Henry's coefficient, Eq. (1) can be transformed into Eq. (2) (1):

$$k = \omega.\Delta[O_3]/([RH].\ \alpha[O_3]_g) \qquad (2)$$

One of the widely applied criteria with respect to the conditions of validity (applicability) of Henry's Law is the expression:

$$D_{O3}.k_1'/k_L^2 << 1$$

where D_{O3} is the diffusion coefficient of ozone in the solution; $k_L=D_{O3}/\delta$ is the coefficient of mass transfer in the liquid phase, and δ is thickness of the boundary layer in the hydrodynamic model of renovation surface; or $k_L=(D_{O3}.s)^{1/2}$, where s is the time interval of renovation. In the case of applying the bubbling method with small bubbles (diameters up to 2.5-3 mm) then $k_L=0.31x(g\nu)^{1/3}x(D_{O3}/\nu)^{2/3}$, where $\nu=\eta/\rho$, is the kinematic viscosity of the solvent, η is the viscosity of the solvent, ρ is the solvent density, g is the earth acceleration. Usually the k_L values are of the order of 0.1-0.05 cm/s. As $k_1`=k[RH]_o$ in most of the cases it is possible to select such values for $[RH]_o$, at which the criterion for applicability of Henry's Law is fulfilled (34).

In order to minimize the influence of the so-called "effect of delay in the response function"– $[O_3]g=f(\tau)$ upon calculating the values of k such sections of the kinetic curves are selected, which appear to be practically parallel or only slightly inclined with respect to the abscissa: $k_1`\alpha[O_3]_g >> d[O_3]_g/d\tau$. The advantages and limitations of this method have been discussed in detail in (37, 38). Despite some contradictory observations, the significant part of rate constants of ozone with organic compounds and polymers are obtained on the basis of Eq. (2) (1, 34).

Results and their discussion

Alcohols

We will start our review with the reactions of ozone with alcohols. A number of authors have tried to elucidate the kinetics and mechanism of the ozonolysis of alcohols and their application to the selective preparation of ketones and aldehydes in high yields under mild conditions (3, 39-46). The basic concepts on such reactions are discussed in several references (1, 2, 25, 34, 35, 39). It has been established that the rate of ethanol ozonolysis does not change when the hydroxyl group is deuterated (43) and its value is 4.17 times higher than that when the methylene group is deuterated. On the basis of this fact, together with the data from the analysis of the product composition and the kinetics of their formation the authors have suggested that the H-atom abstraction by the ozone molecule is the rate-determining step of the reaction. This conclusion is confirmed by the data in Table 1 as reported by various authors (41-43). The ratio between the relative reactivities of tertiary: secondary: primary alcohols is 1:12:241 according to reference (41), or 1:156:817 according to reference (7). On the basis of the studies on the reaction of ozone with methyl, ethyl and 2-propyl alcohol, the following reaction mechanism is proposed (Scheme 1) (40):

$CH_3OH + O_3 \Leftrightarrow [HOC^{\bullet}H_2...HO_3^{\bullet}]^{\#} \rightarrow HOCH_2OOOH$,

and in the presence of a base:

$CH_3OH + O_3 + (B) \rightarrow HOCHO + {}^{-}O_2H + BH^{+}$

$CH_3CH_2OH + O_3 \Leftrightarrow [CH_3HC^{\bullet}(OH)...HO_3^{\bullet}]^{\#} \rightarrow CH_3HC(OOOH)OH \rightarrow$

$CH_3OOH + H_2O_2$ and/or $CH_3CHO + O_2 + H_2O$

$(CH_3)_2C(OH)H + O_3 \Leftrightarrow [(CH_3)_2C^{\bullet}(OH)...HO_3^{\bullet}]^{\#} \rightarrow (CH_3)_2C(OH)OOOH$

$\downarrow -O_2$

$CH_3C(OH)=CH_2 + H_2O + O_2\ (CH_3)_2CO + H_2O$

$\downarrow +O_3$

$CH_3COOH + HCHO$

Scheme 1

It is supposed that an intermediate ion or pair of radicals is formed, whose recombination in the kinetic cage yields α-hydroxy-hydrotrioxide. The latter leaves the cage and passes into the volume of solution.

Table 1 - Kinetic parameters of the ozone reaction with aliphatic alcohols at 25°C

Alcohols	k, $M^{-1}.s^{-1}$	lg A	E, kcal/mol	Reference
t.-Butanol	0.01	4.6	9.0	(32)
t.-Butanol	0.05	-	-	(31)
Ethanol	0.35	6.7	9.8	(32)
Ethanol	0.25 (22 °C)	6.7	9.8	(33)
n-Butanol	0.54	7.3	10.3	(32)
n-Butanol	0.39			(31)
iso-Propanol	0.89	7.3	10.0	(32)
Cyclopentanol	1.35			(31)

The authors of reference (40) found that the product composition of 2-propanol ozonolysis depends on the method of propanol purification. Taking into account the above given consideration about the reaction pathway, in our opinion, the mechanism still remains unclear and new data should be provided for its elucidation. In this connection we have carried out intensive experimental studies on the kinetics of ozonolysis of MeOH, *t*-BuOH, EtOH, *n*-PrOH, *n*-BuOH, *i*-PrOH, *s*-BuOH, *c*-HexOH both by the static and barbotage methods, the results of which are summarized in Figures 1-2 and Tables 2-4.

Figure 1 demonstrates the kinetic data of ozone consumption in solutions of methanol, ethanol and isopropanol by means of the static method with time interval of mixing less than 0.2 seconds. It is seen that regardless of the type of alcohol being ozonized, the kinetic curves coincide with first-order rate law. With a view to more precise evaluation and comparison of the respective rate constants such concentrations of the respective alcohols have been selected, at which the rates of ozone consumption have close values. The kinetic curves of ozone reactions with MeOH, EtOH and i-PrOH gave the following values of the rate constants: 0.057, 0.17 and 1.13 M^{-1}.s^{-1}, respectively.

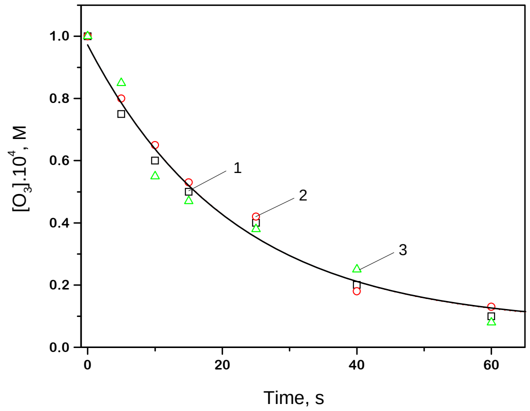


Figure 1 - Kinetics of ozone consumption in the reaction of ozone with: 1 - methanol, 22 °C, 0.74 M; 2 - ethanol, 3 °C, 0.24 M; and 3 - isopropanol, 3.5 °C, 0.037 M

The same values were also obtained by carrying out the reactions in a bubble reactor. The values of *k* are calculated on the basis of Equation 2 – the data are given in Table 2 and they are represented graphically in Figure 2.

Table 2 - Kinetic parameters of ozone reaction with MeOH in carbon tetrachloride (CCl_4) and pure MeOH solutions: 22 °C, ω = 0.167 s^{-1}; v = 1.67 x 10^{-3} L/s, maximum rate of ozone inlet - 1.67 x 10^5 M.s^{-1}

[MeOH], M	$[O_3]_0$ × 10^5, M	$[O_3]_g$ × 10^5, M	Δ$[O_3]$ × 10^5, M	W × 10^6, M.s^{-1}	k, M^{-1}.s^{-1}
1	**2**	**3**	**4**	**5**	**6**
0	10	0	10	0	-
0.247	10	8.32	1.68	2.80	0.057
0.439	10	7.35	2.65	4.43	0.056
0.618	10	6.64	3.36	5.61	0.058
0.740	10	6.22	3.78	6.31	0.055
0.987	10	5.53	4.47	7.46	0.057
1.0	10	5.49	4.51	7.53	0.056
2.0	10	3.79	6.21	10.37	0.055
3.0	10	2.89	7.11	11.87	0.057
4.0	10	2.34	7.66	12.79	0.058
5.0	10	1.96	8.04	13.42	0.054
10.0	10	1.09	8.91	14.88	0.056
24.7	10	0.47	9.53	15.91	0.058
0.740	8	4.98	3.02	5.04	0.057
0.740	6	3.73	2.27	3.79	0.055
0.740	4	2.49	1.51	2.52	0.056
0.740	2	1.24	0.76	1.27	0.058

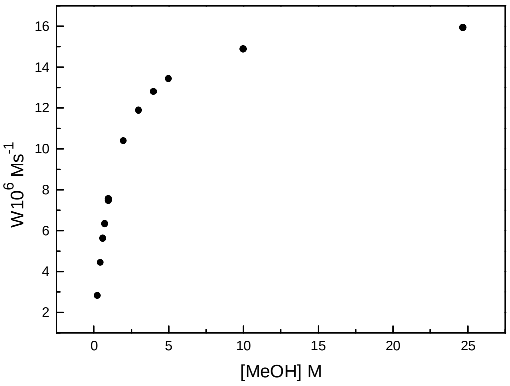


Figure 2 - Dependence of the rate of ozone consumption on methanol concentration at $[O_3]_o$ = 1.10^{-4} M (according to Equation 1)

Processing the data from Table 2, columns 2, 3, and 5, based on Equation 2, yield the linear dependencies of the rate of ozone consumption on the ozone concentrations. The dependence of the rate W on ΔO_3 has also been found out to be a linear one. The dependence of the rate W on the concentration of alcohol [ROH] (column 1) is a curve, which approaches a limit value at W = 1.67 × 10^{-5} M.s^{-1}. The nonlinear character of this relationship is in accordance with the complexity of Equation 2 (see also Figure 2). In the case when $[ROH] \rightarrow \infty$, then we have $[O_3]_g \rightarrow 0$ and $\Delta O_3 \rightarrow [O_3]_o$. The values of *k,* calculated based on Equation 2 at each one of the points on the curve (Fig. 2), are equal to 0.057.

Table 3 - Dependence of *k* on the temperature in °C for ozone reaction with three types of alcohols

k, M^{-1}.s^{-1}	0 °C	10 °C	20 °C	25 °C	30 °C
MeOH	0.008	0.021	0.049	0.072	0.108
t-BuOH	0.005	0.013	0.029	0.045	0.064
EtOH	0.14	0.28	0.54	0.74	1.10
n-PrOH	0.19	0.36	0.67	0.89	1.18
n-BuOH	0.15	0.30	0.56	0.76	1.10
i-PrOH	0.93	1.61	2.71	3.46	4.39
s-BuOH	0.88	1.54	2.58	3.29	4.18
c-HexOH	0.92	1.59	2.65	3.37	4.27

Therefore the experimentally obtained linear dependences of W on $[O_3]_o$, $[O_3]_g$ and on Δ$[O_3]$ as well as the profile of the curve in Figure 2 correspond to the mathematical description of ozonolysis in a barbotage reactor - Equation 2.

Judging from the analysis of the data obtained (Tables 3 and 4) it follows that the rate constant and the activation energies are strongly dependent on the alcohol structure. The interaction of ozone with MeOH possessing primary α-H atoms and with *tert*-BuOH having only primary C-H bonds has been found to be the slowest, and the value of *k* at 20 °C per one α-H atom in the first case is 1.62 × 10^{-2} M^{-1}.s^{-1}, and in the second case, related to one primary H atom, is 3.22 × 10^{-3} M^{-1}.s^{-1}. The difference in the values of these constants is due to the fact that while the OH group in MeOH directly affects the α-H atom, in the case of the *tert*-BuOH, which does not possess any α-H atoms, the effect of the OH groups is transferred through one σ-bond and so it is considerably weaker.

Table 4 - Kinetic parameters of ozone reaction with some alcohols at 25 °C

Parameters	MeOH	*t*-BuOH	EtOH	*n*-PrOH	*n*-BuOH	*i*-PrOH	*s*-BuOH	*c*-HexOH
$k \times 10^2$, $M^{-1}.s^{-1}$	7.2	4.5	74	89	76	346	329	337
n, α-C-H	3	9 (β-C-H)	2	2	2	1	1	1
$k \times 10^2/n$, $M^{-1}.s^{-1}$	2.4	0.5	37	44	38	346	329	337
E_a, kcal/mol	13.9	13.7	10.9	10.1	10.4	8.5	8.5	8.4
$A \times 10^{-7}$, $M^{-1}.s^{-1}$	41	5.8	3.9	2.4	1.7	0.62	0.59	0.51

As a result of this, the reactivity of *tert*-BuOH becomes similar to that of methane and neopentane. The interactions of ozone with EtOH, *n*-PrOH, *n*-BuOH take place at higher rates and the values of *k* per one α-H atom amount to: 0.27, 0.34 and 0.28, respectively. The higher rates of the ozone reactions with these alcohols are associated with the presence of secondary α-H atoms in their molecules, which have lower bond energies than the primary ones. The enhanced reactivity of *n*-PrOH compared with that of EtOH could be assigned to the donor effect of the second CH_3 group while the donor effect of the C_2H_5 group in *n*-BuOH is weaker than that of the methyl group and therefore *k* is lower. It has been found that the reactions of ozone with *i*-PrOH, *s*-BuOH and *s*-HexOH alcohols possessing *tert*-H atoms with the lowest bond energies is the fastest with *k* equal to 2.71, 2.58 and 2.65, respectively, i.e., in fact they are almost the same. The ratio between the reduced values of *k* at 25 °C for methanol: ethanol: *sec*.butanol are 1:15:137. Simultaneously, the values of E_a decrease with the decrease of the α-H atoms bond energy (D) and their ratio is 1:0.78:0.61 (12, 15). This fact can be regarded as important evidence for the mechanism of α-C-H-atom abstraction by ozone.

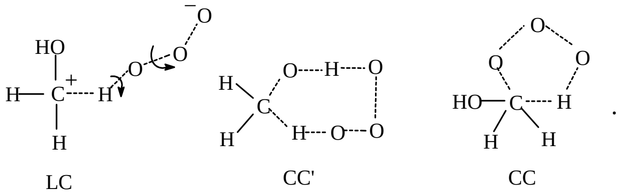


Figure 3 - Structure of the probable activated complexes in the reaction of ozone with aliphatic alcohols: LC - linear with free fragment rotation and CC′ and CC - cyclic complexes without free rotation

The theoretical estimates of A were performed considering the two possible structures of the activated complex (AC): linear (LC) and cyclic (CC) (Figure 4). The good agreement between the experimental data and theoretical estimates for A allows the determination of the AC structure and on this basis enables the selection of the most probable mechanism. Simultaneously the value of the pre-exponential factor was calculated by the collision method and by comparing its value with the one calculated based on the AC theory the steric factor – p was determined (Equation 3) (48-52):

$$k = p.Z_0.\exp(-E_a/RT), \qquad (3)$$

where: $Z_0 = \pi.(r_A+r_B)^2 \times (k_B\ T/\pi m^*)^{1/2}$; Z_o is the collision factor; r_A and r_B are the van der Waals radii of the reagents; k_B is Boltzmann's constant; T is the absolute temperature; and m^* is the reduced mass.

The pre-exponential factors for the reactions of ozone with alcohols, calculated according to the activated complex method (ACT) and collision theory (CT) are represented in Table 5.

Table 5 - The values of A calculated by ACT with LC and CC and by CT, the sums (R_{fr}) and energy (E_{fr}) of inner rotation, steric factors (p), VDW radii of the molecules (r) and the ratio between the calculated and experimental values of pre-exponentials A^{LC}_{cal}/A_{obs}

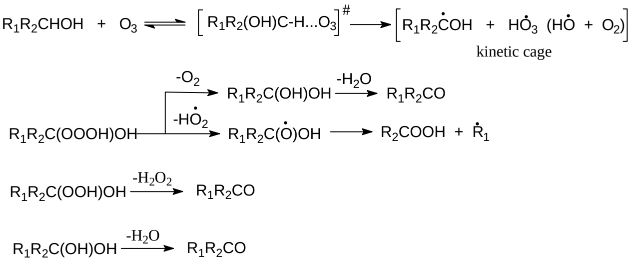
Parameters	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	*s*-BuOH	*t*-BuOH	*c*-HexOH
$A^{CC} \times 10^{-4}$, $M^{-1}.s^{-1}$	52	8.3	3.7	3.5	2.4	2.2	6.3	1.6
$A^{LC} \times 10^{-4}$, $M^{-1}.s^{-1}$	56	15	6.7	6.3	4.4	4.0	4.9	2.9
$F_{fr} \times 10^{-2}$	7.1	9.8	12	11	13.8	12.6	12.9	12.6
$A^{LC}_{cal} \times 10^{-7}$, $M^{-1}.s^{-1}$	40	15	8.1	6.8	6.1	5.0	6.3	3.6
r, Å	2.24	2.57	2.91	2.88	3.13	3.23	3.13	3.23
$A^{CT} \times 10^{-11}$, $M^{-1}.s^{-1}$	2.6	2.6	2.7	2.7	2.8	2.8	2.8	2.7
$p \times 10^5$	22	5.8	2.5	2.3	1.6	1.4	1.8	4.1
A^{LC-}_{cal}/A_{obs}	1.0	3.8	3.4	11	3.1	8.3	1.1	7.2
$E_{fr,}$ cal/mol	0	730	670	1368	701	1172	52	1081

Note: ALC is the pre-exponential factor calculated with LC without free fragment rotation (it is absent at $E_{fr} \geq 4$ kcal); A_{CC} – calculated with CC; A^{LC}_{calc} = at free fragment rotation, i.e., when $\exp(-E_{fr}/RT) = 1$ or $E_{fr} = 0$ kcal; A_{ct} – calculated according to the collision theory at 300 K and r – calculated by the Alinger method (*PCMOD4* program) at the radius of the ozone molecule of 2A; E_{fr} – the calculated values of the rotation energy at ratio of $A^{LC}_{cal}/A_{obs} = 1$.

An interesting fact is the good agreement between the values of A^{LC} and A^{CC}. The values of A^{CC} with the five- and seven-member cyclic form of AC are practically similar as they differ by not more than 1%. However the free rotation produces an increase in A^{LC}_{cal} by three orders of magnitude compared with that of A^{CC}. The steric factor has a value, which is in agreement with a liquid phase reaction. The ratio between the calculated and experimental values of A^{LC}, is increasing in the sequence primary: secondary: tertiary alcohols is 1:3.4:8.8, i.e., the coincidence in this sequence is decreasing. This is connected with the fact that E_{fr} is not zero and it is increasing with the changes in the alcohol structure in the same sequence. It has been found that the values of A^{LC}_{calc} and A_{obs} coincide when the values of rotation energy are those given in line 10 in Table 5. We have obtained the same values by means of the *MOPAC 6* software package and therefore the data on the free rotation energy (E_{fr}) in line 10 can also be considered as theoretically evaluated.

The good agreement between A^{LC}_{calc} and A_{obs} suggests that the rate-determining step of the ozone reaction with alcohols involves the formation of linear AC and abstraction of the α-H atom from the alcohol molecule.

The experimental and theoretical results conform well to Scheme 2.



Scheme 2

Ozone attacks the α-H atom, forming a LC, which further undergoes decomposition into a radical (or ion) pair in one kinetic cage. The α-hydroxy alcohol, α-hydroxyperoxy alcohol and α-hydroxytrioxy alcohol being unstable leave the cage and decompose rapidly to the corresponding aldehyde or ketone liberating water, hydroperoxide and oxygen or lead to the formation of hydroperoxy and alkoxy radicals. The latter species can further undergo monomolecular decomposition.

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