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REACTIONS OF OZONE WITH ALCOHOLS, KETONES, ETHERS AND HYDROXYBENZENES (PART 4)

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 spectro-photometrically 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):

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

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):

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

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

Hydroxybenzenes

Reactions of ozone with alcohols and ketones were considered in the previous parts of the review (39-41). The reactions of ozone with mono- and dihydroxybenzenes have provoked so far a particular interest (42-50), namely, because of their great importance for environment protection, chemical stabilization and the theory of reactivity. The ozonation of phenol, pyrocatechol, resorcinol and hydroquinone has been studied in different solvents – aqueous and organic, aimed at the deriving of the kinetic parameters and product composition (51-61). The rate constants of phenol and resorcinol ozonation in water at room temperature are 1.3×10^3 $M^{-1}.s^{-1}$ and $>3\times10^5$ $M^{-1}.s^{-1}$, respectively, whereas the rate constants of benzene, toluene and anisole ozonation in organic media are 2, 14 and 2.9×10^2 $M^{-1}.s^{-1}$ (45-47, 62).

Gurol and co-workers (48) found that the relative rates of pyrocatechol/phenol and resorcinol/phenol ozonation in water medium are 220 and 70, respectively. Provided that the rate constant of phenol ozonation is known (47), the calculated values of the rate constants of pyrocatechol and resorcinol ozonation are 2.86×10^5 $M^{-1}.s^{-1}$ and 9.1×10^4 $M^{-1}.s^{-1}$, respectively. However, in the case when the reaction is carried out in organic solvents the values are quite different. For example, in CCl_4 and at room temperature the following values have been obtained for: benzene - 0.06, ethylbenzene - 0.2, anisole - 1.1, phenol - 230 and pyrocatechol - 3.2×10^3 $M^{-1}.s^{-1}$ (45, 62-64). One of the possible explanations for the different values of the rate constants of hydroxyphenols ozonation obtained by the various researchers could be the great influence of the water on this reaction, for example for phenol they vary within the range 100-180 $M^{-1}.s^{-1}$, 500 $M^{-1}.s^{-1}$ for pyrocatechol and 300 $M^{-1}.s^{-1}$ for 3,6-di-*tert*-butylpyrocatechol. Pryor and co-workers (62) have reported that the rate constants of ozone reaction with α-tocopherol in CCl_4 and water are 5.5×10^3 $M^{-1}.s^{-1}$ and 1×10^6 $M^{-1}.s^{-1}$, with α-tocopherol acetate - 1.45×10^2 $M^{-1}.s^{-1}$ and for the reaction with α-tocopherolquinone it is 1.15×10^4 $M^{-1}.s^{-1}$.

Ozone is unstable when dissolved in water. The mechanism and the kinetics of the elementary reactions, involved in the ozone decomposition, have been investigated in numerous studies (65, 66, and references therein). The stability of the ozone depends to a great extent on the water matrix, especially on its pH value. The pH of the water is important because the hydroxide ions initiate ozone decomposition, which involves the following reactions (65):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\ M^{-1}\ s^{-1} \quad (1)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \qquad k = 2.8x10^6\ M^{-1}\ s^{-1} \quad (2)$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \qquad k = 1.6x10^9\ M^{-1}\ s^{-1} \quad (3)$$

In aqueous solution the ozonide radical decomposes quickly into an OH radical, O_2 and OH anion (65, 66).

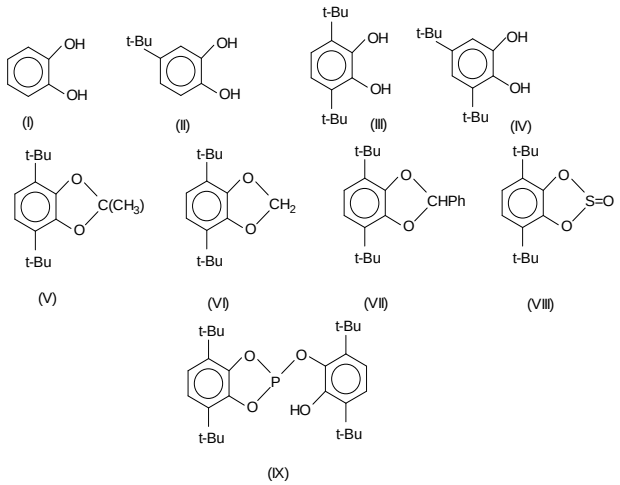
Additionally in the case of ozone reaction with electron-rich compounds, such as phenols (phenolates) and akoxylated aromatics in aqueous phase again OH radicals are formed, most probably via the mechanism of formation of the respective ozone adduct (66, 67). For example it has been established that as a result of the electron transfer from phenol to ozone (reaction 4) at neutral pH the radical anion O_3^- is obtained with an yield of 22% (68).

$$PhO^- + O_3 \rightarrow PhO^{\bullet} + O_3^{\bullet -} \quad (4)$$

As a result the rate constant of one and the same compound (of phenols or alkoxylated aromatics type) in water, determined on the basis of its ozone consumption, varies within a wide range of values depending on the pH values, and on the presence of hydroxyl radical scavengers minimizing the interfering radical chain reactions. This rate constant differs from that one, determined on the basis of the compound consumption (69). However, this aspect requires special studies and discussion, which are beyond the scope of the present investigation.

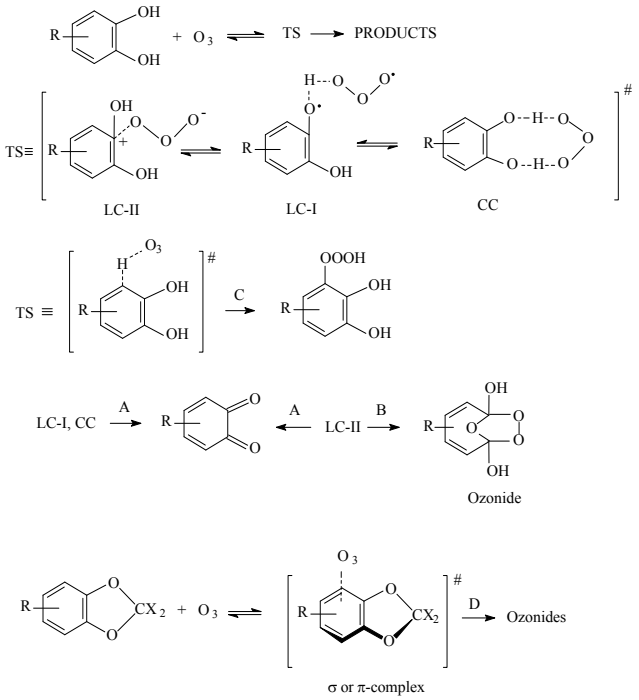
Product analysis of pyrocatechol ozonation in aqueous medium shows that 3 moles of ozone are readily absorbed to give CO_2 (24.8%), CO (6%), formic acid (32.5%) and glyoxal (4.2%). As CO_2 and formic acid are the main reaction products, it seems very likely that most of the pyrocatechol undergoes anomalous ozonolysis (57). Radical formation has been observed during 2,6-di-*tert*-butylphenol ozonolysis. When the ratio of absorbed ozone to phenol is 0.8, 50% viscous yellow oil and 3,5, 2,6-di-*tert*-butyl-*o*-quinone have been identified in the products (60). In 3,6-di-*tert*-butyl-pyrocatechol ozonation the corresponding quinone was found to be the main product after complete consumption of the initial substrate (61). Side products such as 2,5-di-*tert*-butyl-, 3-hydroxy-*p*-quinone and 3,6-di-*tert*-butyl-1,2-phenylacetal-5-hydroxy-3,6-di-*tert*-butyl-*p*-benzophenone have also been found. The rate constant of this reaction amounts to 3×10^2 $M^{-1}.s^{-1}$. The same constant with the corresponding pyrocatechol with O-hydroxy-acetylated groups has been estimated to have a two orders of magnitude lower value. A mechanism has been supposed to involve the formation of either a 1,3-cyclic activated complex between two hydrogen atoms from two OH groups and one ozone molecule or π- or σ-complexes, formed with the benzene ring.

The different values of the literature constants and the various mechanisms proposed for this reaction impose the necessity of further research of its kinetics and reaction pathway. In this connection we have studied the ozonolysis of the following hydroxybenzenes (Scheme 1).



Scheme 1

The probable mechanisms of ozone interaction with dihydroxybenzenes are represented in Scheme 2.



Scheme 2

The mechanism A with a cyclic complex (CC) formation in the transition state was supposed by Razumovskii and co-workers (61). The mechanism B with linear complex LC-II in the transition state was put forward and discussed by Bailey (43). The interaction of ozone with C-H bonds with the formation of trioxide (45, 64) as a possible parallel reaction is indicated in mechanism C. The acetylated forms of dihydroxybenzenes can react only via attack on the benzene ring according to mechanism D or C. Formally, mechanism D can be regarded as an extended version of mechanism B, involving the formation of TS similar to π- or σ-complexes. We propose a new mechanism, an extended version of the Razumovskii mechanism, whereby the transition state is linear with LC-I structure.

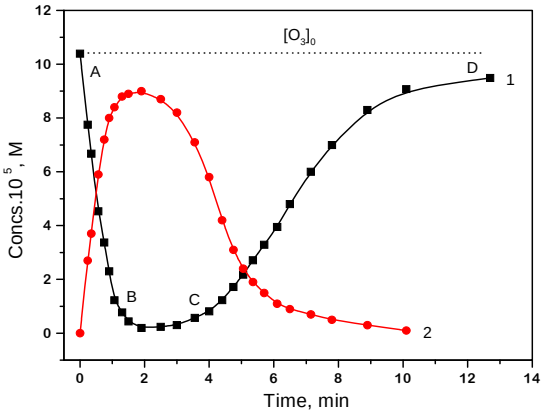


Figure 1 - Kinetic curves of ozone absorption at reactor outlet (1) and *o*-quinone accumulation (2) in the course of pyrocatechol ozonation at ambient temperature, [PC] = 0.227 mM in CCl_4 (10 ml) during bubbling of ozone with 0.1 L/min flow rate

Upon ozonation of any of the investigated catechols directly inside the electron spin resonance cell or after freezing the reaction products in liquid nitrogen no signals have been detected.

The kinetic curve of the changes in the ozone concentration at the bubbling reactor outlet (Figure 1, curve 1) is characterized by three different regions: AB – fast ozone consumption after the addition of pyrocatechol, BC – steady-state part, when the rate of the chemical reaction becomes equal to the rate of ozone supply, and CD – the ozone concentration begins to rise up due to the pyrocatechol consumption. The BC part of the curve allows calculation of the rate constant, and based on the area below the curve ABCD – evaluation of the stoichiometry of the reaction. The straight line designated $[O_3]_0$ is the ozone concentration at the reactor inlet. Curve 2 presents the *o*-quinone formation in the course of the reaction time. Its profile suggests the intermediate formation of *o*-quinone.

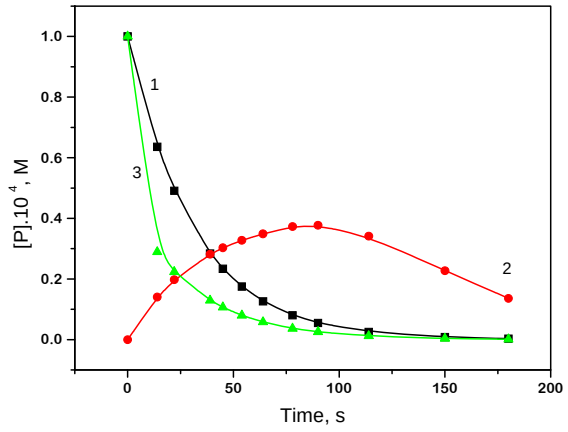
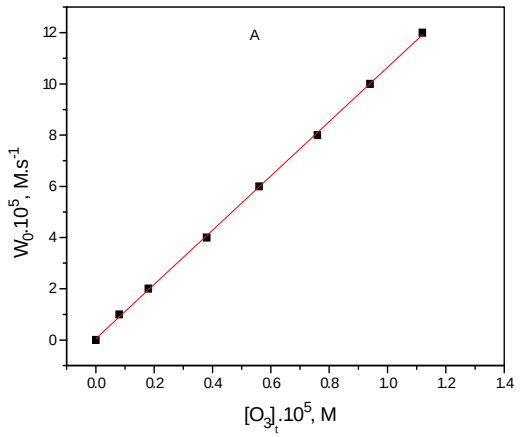


Figure 2 - Kinetics of pyrocatechol consumption (1), *o*-quinone accumulation (2) and *o*-quinine consumption (3), at ambient temperature, $[O_3] = 1\times10^{-5}$ M

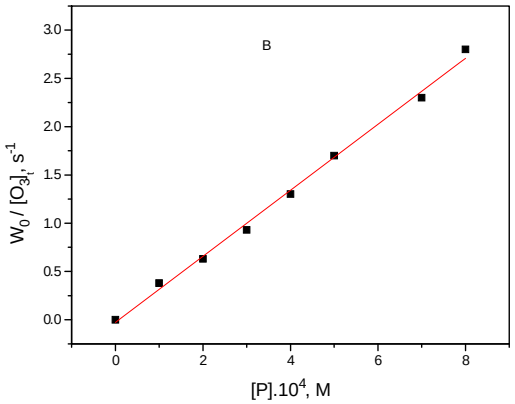
The kinetic curves of the product formation in pyrocatechol ozonolysis, its consumption and *o*-quinone consumption during its ozonation in a separate experiment are given in Figure 2. The rate constants of pyrocatechol and *o*-quinone consumption, calculated based on the kinetic curves in Figure 2, were 3.2×10^4 $M^{-1}.s^{-1}$ and 7.1×10^4 $M^{-1}.s^{-1}$, respectively. The initial rate of the *o*-quinone formation had almost the same value as that of pyrocatechol consumption. The small variation of the constants is due to the participation of pyrocatechol in parallel reactions. Actually, during the reaction small amounts of open-chain products have been identified.

Pyrocatechol ozonation at 15% conversion degree gave the following yields: *o*-quinone - 85%, pyrogallol - 3%, ozonide - 10%, muconic acid - 2%, maleic acid and fumaric acids and the polymeric products - 1%. The ratio between the amount of absorbed ozone and the consumed pyrocatechol was calculated to be 6. Similar ratio values have also been obtained for the other hydroxybenzenes with free hydroxy groups.

It was found that with the increase of the conversion degree from 0 to 100%, the amount of open-chain products is continuously increasing, while that of the remaining products passes through a maximum. The individual compounds identified by ^{13}C-NMR are: muconic semialdehyde and acid - 20%, maleic and fumaric semialdehyde and acid - 40%, glyoxal, formic acid, oxalic acid, carbon dioxide and polymeric products - 40%. The reaction rate of dihydroxybenzene ozonation follows first-order kinetics in relation to each reagent (Figures 3 a and 3 b).



a



b

Figure 3 - Dependence of the rate of pyrocatechol ozonation on the concentration of ozone (a) and on the concentration of pyrocatechol (b)

Table 1 represents the obtained experimental kinetic data on the ozonation of the investigated dihydroxybenzenes at various temperatures.

A drastic difference between the values of the kinetic parameters of catechols I-IV and V-IX, in which the OH groups are acetylated, has been observed. The rate constants of catechols I-IV manifested 4-28 times higher values than those of catechols of V-IX types. On the other hand the pre-exponential factors demonstrated with about two orders of magnitude lower values with the former compounds. The activation energies are 2.05±0.5 and 5.9±0.5 kcal/mol, respectively, or the acetylation of the HO groups leads to an increase in E_a by about 4 kcal/mol. The ozone probably reacts predominantly with the hydrogen atoms of the HO groups and, only to a very small extent, with the benzene ring. The ratio of these ozone interactions

varies from 94:4 to 80:20 depending on the hydroxybenzene nature. The lower activation energies of catechols I-IV with respect to those of V-IX are more consistent with the formation of an activated complex of contact type in the transition state, i.e., with structure LC-I (Scheme 2). This assumption could also be confirmed by the analysis of the kinetic parameters of the ozonation of anizol, benzenes, phenol and toluene. The reaction of ozone with benzene proceeds at a low specific rate of 0.06 $M^{-1}.s^{-1}$ and a relatively high activation energy equal to 12.8 kcal/mol. The methyl derivatives of benzene, i.e., toluene, reacts 6.7 times faster and the E_a is decreased by 2.5 kcal/mol, and the rate of anizol ozonation is even higher - 10 $M^{-1}.s^{-1}$. The exchange of ketyl group by a hydroxyl one leads to significant acceleration of the ozonation reaction rate and it approaches values of 160 $M^{-1}.s^{-1}$, and the activation energy is reduced by 5.8 kcal/mol. Probably, in this case the mechanism of the reaction is changed and ozone interacts predominantly with the hydrogen atoms of the OH groups. The decrease in the reactivity of anizol compared with that of phenol (~16 times) supports this assumption.

Table 1 - Kinetic data of dihydroxybenzene ozonolysis in CCl_4, 20°C

Substrate	*k*, $M^{-1}.s^{-1}$	lg A	E_a, kcal/mol
I	3230	5.35	2.5
II	3100	4.91	1.9
III	3100	5.07	2.1
IV	3200	4.80	1.7
V	500	7.14	6.0
VI	749	7.17	5.8
VII	828	7.06	5.6
VIII	598	6.84	5.5
IX	111	6.81	6.4
Benzene	0.06	8.32	12.8
Toluene	0.40	7.05	10.3
Anisole	10	-	-
Phenol	160	7.31	7.0

The analysis of the kinetic parameters of catechols in acetylated form and those of benzene, toluene, anizol and phenol shows that the rate constants increase and the activation energies go down upon increasing the number of the electron-donating substituents (Table 1). The high values of the pre-exponential factors could be associated with the high values of the energy of free rotation in the activated complex as a result of the steric hindrances caused by the presence of the bulky *tert*-butyl groups. This means that in the case when the hydroxyl groups are acetylated, the activated complex should have an LC-II like structure and the ozonation would lead only to the formation of ozonides and open ring products.

The kinetic parameters of some dihydroxybenzenes have been determined in the case of ozonation in aqueous medium (for those ones, which are water soluble - I-IV, VIII and IX). However, we have found that because of the diffusion limitations in the bubbling reactor we have not been able to measure constants higher than 1×10^4 $M^{-1}.s^{-1}$. In fact, the literature values for some of these constants are of this order, but they have been measured by a modified stop-flow technique (70).

The analyses made so far show that the reaction path of the ozone reactions with dihydroxybenzenes depends strongly on their nature and they precede via transition states with activated complex - LC-I or LC-II. The parameters needed for the calculations are represented in Table 2.

In addition, we have calculated the heats of formation of pyrogallol – -117.6 kcal/mol (-129 kcal/ mol [(71)]), 3-trihydroxy pyrocatechol – -59 kcal/mol, H_2O_3 – -21.2 kcal/mol (-17.7 kcal/mol [(71)]) and ozone - 34.1 kcal/mol.

Thus, the heats of the ozonation reaction according to the different mechanisms have been calculated and they amount to the following values: A - 33.1; B and D - 46.1 and C - 32.1 kcal/mol. All the mechanisms are exothermic and, therefore thermodynamically favorable. In this case only the magnitude of the activation energy and the entropy benefits will determine the reactivities of these compounds and the reaction pathway.

Table 2 - Symmetry numbers (σ), VdW radii (r), heats of formation (ΔH) of dihydroxybenzenes and the corresponding quinones and ozonides

Substrate	σ	r, Å	ΔH, kcal/mol	$\Delta H^{quinone}$, kcal/mol	$\Delta H^{ozonide}$, kcal/mol
I	2	3.02	-62 (-85)	-39 (-43)	-73
II	1	3.82	-88	-66	-99
III	2	4.46	-109	-86	-125
IV	1	4.39	-110	-90	-123
V	2	5.07	-116		-125
VI	2	4.56	-90		-103
VII	1	5.37	-63		-86
VIII	1	4.77	-73		-77
IX	1	5.30	-135		-140
Benzene	6	2.86	19 (13)		21
Toluene	1	3.37	12 (3)		11
Anisole	1	3.45	-16 (-26)		-20
Phenol	1	2.96	-21 (-38)		-24

Note: The experimental values are in parentheses (71).

Table 3 - Calculated pre-exponential values for ozone reaction with dihydroxybenzenes

Substrate	lg A, TC	lg A, CC	lg A, LC	lg A, calc.	A_{calc}/A_{obs}	lg p
1	2	3	4	5	6	7
I	11.318	4.346	7.69	5.39	1.10	5.928
II	11.422	3.905	7.25	4.95	1.10	6.472
III	11.500	4.070	7.42	5.12	1.12	6.380
IV	11.490	3.780	7.12	4.82	1.05	6.670
V	11.572	4.017	7.36	7.36	1.66	4.212
VI	11.511	4.056	7.40	7.40	1.70	4.102
VII	11.801	3.934	7.28	7.28	1.66	4.521
VIII	11.533	3.717	7.06	7.06	1.66	4.473
IX	11.575	3.689	6.88	6.88	1.10	4.695
Benzene	11.319	5.124	8.47	8.47-	1.41	2.849
Phenol	11.322	4.196	7.54	7.54	1.70	3.782

Note: p is the collision factor

Calculated pre-exponential factors (Table 3) were compared with those obtained experimentally (Table 1) and it is seen that A have lower values (~10 times) for the cyclic form of the activated complex, if compared with the experimental values. At the same time the values of A for LC are about 200 times higher. The values of A for CC are the highest as predicted by the theory and they are lower than the experimental values. This supposes that the reaction takes place via a cyclic complex. The values of A calculated for LC in Table 3 have been obtained without taking into account the energy of free rotation. The latter was calculated as a sum of the rotation around H-O and O-O axes (by *mopac6*) and it amounts to 3.1 kcal. This means that the real values in column 4 are about 200 times smaller. The comparison between the A values corrected in this way and the experimental data for the compounds I-IV reveals complete agreement.

The reaction pathway of the ozonation reactions of compounds V-IX is quite different as the transition state includes the formation of a σ- or π-complex. For these compounds the formation of AC in the transition state is impeded due to the breaking of their aromatic character but simultaneously the free rotation is facilitated, whose energy may be even zero, due to the action of the principle of the lowest energy. If the energy of free rotation is assumed to be very low then the values of A calculated for LC-II would coincide with the experimentally found ones. Such a coincidence is observed for compound V in column 5 (Table 3).

The basic conclusion from the analysis of the results obtained for this reaction is that the kinetics and mechanism of the ozonation reaction of dihydroxybenzenes depend strongly on their structure and the type of the reaction medium.

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