2008 Russian Chemical Bulletin, International Edition, Vol. 56, No. 10, pp. 2008—2013, October, 2007

Kinetics of gas—liquid ozonization of veratrole and its derivatives

A. G. Khudoshin,* A. N. Mitrofanova, and V. V. Lunin

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 4575. E-mail: khudoshin@kge.msu.ru

The kinetics was studied for the reactions of ozone with model lignin compounds, *viz.*, phenol, veratrole, veratric aldehyde, and veratric alcohol. Using the mass transfer model for a chemical reaction based on the film theory, the reaction rate constants were calculated. The reaction rate constants determined by both the ozone absorption rate and changes in the substrate concentration coincide satisfactorily, indicating adequacy of the kinetic model chosen. A relationship between the structure of the compounds under study and their reactivity was found.

Key words: model lignin compounds, ozonization, phenol, veratrole, veratric aldehyde, veratric alcohol, kinetics, film model, reaction rate constants.

Investigation in the areas of conversion of vegetable matter has intensely been developed in recent years. Lignin is the major component of the plant raw materials. One of promising routes is the oxidative destruction of lignin by ozone, which is highly reactive toward aromatic and unsaturated compounds.

The reaction of ozone with lignin is of interest from the viewpoint of designing new technologies for delignification and cellulose bleaching, waste water treatment in pulp and paper industry, and production of valuable products from lignin.

Lignin is a natural polyfunctional phenolic polymer with an irregular structure. To study the kinetics and mechanism of its ozonization, researchers often use compounds modeling different structural fragments of lignin, for example, compounds of the guaiacyl, syringyl, and veratryl series with various substituents.[1,2]

The purpose of this work is to study the reactivity of various compounds of the veratryl series. For this purpose, we studied the kinetic regularities of the oxidation with ozone of the simplest model lignin compounds: phenol, veratrole, veratric alcohol, and veratric aldehyde.

The film model is frequently used[3,4] to determine the kinetic parameters of the mass transfer-controlled reactions in gas—liquid systems. From the viewpoint of this model, it is necessary to reveal the region where the reaction occurs: near the interface (in the film) or in the liquid bulk. Depending on the reaction regime, it is significant to choose correctly an appropriate kinetic equation for the description of experimental data.

Experimental

The reactions of ozone with organic compounds were studied on a setup described previously.[5] Ozone was generated from air on a laboratory glass ozonator in a silent discharge (frequency 7 kHz, $I = 40$ mA, $W = 4$ kW).

The ozone concentration in a gas mixture at the inlet and outlet of the reactor was determined using a Medozon 254/3 ozonometer by the optical absorption of ozone at $\lambda = 254$ nm.

Ozonization was carried out at 298 K, an initial ozone concentration of $0.9—1.1 \cdot 10^{-3}$ mol L^{-1}, and the flow rate w = 25 L h^{-1}. The volume of the reaction mixture was 0.55 L.

A gaslift unit with the natural circulation of the liquid phase was used as a reactor.[6,7] This unit was a well-stirred reactor with respect to the liquid phase. An ozone—air mixture was continuously injected through a nozzle into the reaction chamber. A separator with the tangential infeed was used to separate a gas—liquid mixture. The liquid phase was returned through a circulation tube into the reaction zone. Directional circulation was induced in the reactor due to the difference in densities in the reaction and circulation zones.

Ozonization was carried out as follows. A solution in the reactor was saturated with ozone until the steady-state ozone concentration was achieved, and an ozonized substance was introduced. The end of the reaction was accepted to be the coincidence of the ozone concentrations at the inlet and outlet of the reactor.

The substrates were phenol ($3 \cdot 10^{-4}—4 \cdot 10^{-2}$ mol L^{-1}), 1,2-dimethoxybenzene (veratrole) ($2 \cdot 10^{-4}—4 \cdot 10^{-2}$ mol L^{-1}), 3,4-dimethoxybenzaldehyde (veratric aldehyde) ($3 \cdot 10^{-5}—2 \cdot 10^{-2}$ mol L^{-1}), and 3,4-dimethoxybenzyl alcohol (veratric alcohol) ($3 \cdot 10^{-4}—1 \cdot 10^{-2}$ mol L^{-1}) (Aldrich). The reaction with ozone was studied in aqueous solutions of sulfuric acid (pH = 1.5). The reaction course was monitored by pe-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1941—1946, October, 2007.

riodical sampling. The samples were analyzed spectrophotometrically (Cary 3E instrument, Varian, USA) and by HPLC (Agilent 1100 chromatograph with the spectrophotometric detector at the wavelength 270 nm, Zorbax C-18 column, acetonitrile—water—1% phosphoric acid mixture as a mobile phase). Chromatographic analyses were carried out in the gradient regime according to the scheme presented below

t/min	MeCN : H_2O : H_3PO_4
0—4.5	30 : 69 : 1
4.5—8	30 : 69 : 1—60 : 39 : 1
8—9	60 : 39 : 1
9—10	60 : 39 : 1—30 : 69 : 1

Kinetic model

The model based on the film theory[3] is most convenient to study mass transfer-controlled processes. Using this model, it is assumed that a film is formed near the interface and ozone can penetrate through the film only due to molecular diffusion.

Let us consider in more detail the film model for the reaction of ozone with a solution of an organic substance in an ideal-mixing reactor.

$$(O_3)_g \rightleftharpoons (O_3)_l,$$

$$(O_3)_l + B \longrightarrow P,$$

where $(O_3)_g$ and $(O_3)_l$ is ozone in the gas phase and in the solution, respectively; B is the oxidized substance; P is the reaction product.

The system of differential equations for the processes that occur can be written in the form

$$\begin{cases} D_{O_3}\dfrac{d^2[O_3]}{dx^2} = \dfrac{d[O_3]}{dt} + k[O_3][B] \\ D_B\dfrac{d^2[B]}{dx^2} = \dfrac{d[B]}{dt} + k[O_3][B] \end{cases} \qquad (1)$$

with the following boundary conditions: $[O_3]^* = [O_3]_g^* \cdot K$, $d[B]/dx = 0$ for $x = 0$, *i.e.*, an equilibrium ozone concentration is established at the interface, and the substrate does not transfer to the gas phase; $[O_3] = \text{const}$ for $x \geq \delta$, *i.e.*, convection mixing occurs and the ozone concentration is constant in the liquid bulk.

Here D_{O3} and D_B are the diffusion coefficients of ozone and an organic substance, respectively; k is the chemical reaction rate constant; $[O_3]$ and $[B]$ are the concentrations of ozone and an oxidized substance in the solution.

The left part of the system of differential equations (1) describes the diffusion of ozone and the oxidized substance, and the right part describes the change in the concentration (accumulation) and the chemical reaction.

The rate of ozone absorption per surface unit (absorption rate) $\bar{V}$ is determined as follows:

$$\bar{V} = \left.\frac{d[O_3]}{dx}\right|_{x=0}. \qquad (2)$$

The approximate solutions of the system of differential equations (1) for different regimes of the process depending on the reaction rate constant, diffusion coefficients, and ozone and substrate concentrations have been described earlier.[3,4,8]

When the processes occur in the volume of the liquid phase, the absorption rate is determined by the mass transfer coefficient k_L and the difference between the ozone concentrations at the interface $[O_3]^*$ and in the liquid bulk $[O_3]$ according to the equation

$$\bar{V} = k_L a([O_3]^* - [O_3]), \qquad (3)$$

where a is the specific surface of the interface. In this case, the ozone absorption rate is equal to the chemical reaction rate

$$k_L a([O_3]^* - [O_3]) = k[B][O_3]. \qquad (3')$$

This makes it possible to determine the dependence of $\bar{V}$ on the substrate concentration [B]

$$\bar{V} = k_L ak[B][O_3]^*/(k[B] + k_L a), \qquad (4)$$

and to determine the reaction rate constant under certain conditions. At low substrate concentrations ($k[B] \ll k_L a$) the reaction occurs in the kinetic region

$$\bar{V} = k[B][O_3]^*. \qquad (5)$$

With an increase in the concentration $k[B] \gg k_L a$, the process is limited by ozone diffusion and the absorption rate is independent of the substrate concentration

$$\bar{V} = k_L a[O_3]^*. \qquad (6)$$

Under the conditions of high substrate concentrations, ozone has no time to transfer to the liquid phase and reacts entirely in the film. To describe such processes, the acceleration coefficient E is introduced, which shows an increase in the absorption rate due to the chemical reaction in the film

$$\bar{V} = k_L a[O_3]^* E. \qquad (7)$$

The analytical solution of the initial system of differential equations (1) is known only for pseudo-first-order processes.

The approximate solution of the system of differential equations (1) was obtained for second-order reactions, where it is assumed that the reaction occurs in the film and $[O_3] = 0$. The solution takes the form

$$E = \frac{\sqrt{Ha^2(E_i - E)/(E_i - 1)}}{\mathrm{th}\sqrt{Ha^2(E_i - E)/(E_i - 1)}}, \quad (8)$$

where *Ha* is the Hatta number

$$Ha = \sqrt{D_{O_3}k[B]}/k_L, \quad (9)$$

and E_i is the acceleration coefficient of the instant reaction

$$E_i = 1 + D_B[B]/(D_{O_3}[O_3]^*). \quad (10)$$

To determine the rate constants of the chemical reaction, it is necessary to determine the *Ha* value by Eq. (8) using the *E* and E_i coefficients calculated from the experimental data.

Results and Discussion

The plots of the ozone concentration at the reactor outlet *vs* duration of veratric alcohol ozonization at its different concentrations are shown in Fig. 1.

The absorption rate was calculated from the kinetic curves (see Fig. 1) at the time moment $t = 150$ s, when the steady-state ozone concentration is established, according to the equation[9]

$$\bar{V} = ([O_3]_{in} - [O_3]_{out})w', \quad (11)$$

where w' is the specific flow rate, and $[O_3]_{in}$ and $[O_3]_{out}$ are the ozone concentrations at the inlet and outlet of the reactor, respectively.

The plot of the rate of ozone absorption $\bar{V}$ *vs* $\sqrt{[B]_0}$ ($[B]_0$ is the initial substrate concentration) is shown in Fig. 2.

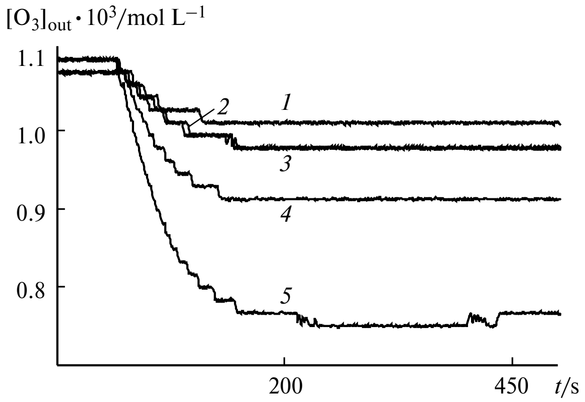

Fig. 1. Kinetics of changing the ozone concentration at the reactor outlet at different ozonization durations and veratric alcohol concentrations $3.8 \cdot 10^{-4}$ (*1*), $5.5 \cdot 10^{-4}$ (*2*), $1.4 \cdot 10^{-3}$ (*3*), $4.4 \cdot 10^{-3}$ (*4*), and $1.2 \cdot 10^{-2}$ mol L^{-1} (*5*).

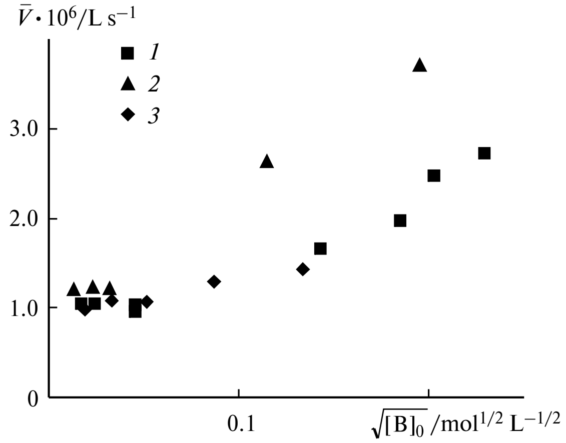

Fig. 2. Plots of the ozone absorption rate *vs* $\sqrt{[B]_0}$ for phenol (*1*), veratrole (*2*), and veratric aldehyde (*3*).

For the calculation of the kinetic parameters of the reactions of ozone with the substrates under study, we used the earlier published diffusion coefficients for ozone in water $D_{O_3} = 1.74 \cdot 10^{-9}$ m^2 s^{-1},[7,10] the mass transfer coefficient for ozone $k_L = 2.8 \cdot 10^{-4}$ m s^{-1},[11,12] and the diffusion coefficients for phenol, veratrole, veratric alcohol, and veratric aldehyde $D_B = 0.9 \cdot 10^{-9}$ m^2 s^{-1} (see Ref. 13).

The ozone concentration on the film surface was determined by Henry's law

$$[O_3]_g = \alpha[O_3]^*, \quad (12)$$

where α is the Henry coefficient. The ozone concentration in the gas phase $[O_3]_g$ was determined by the formula

$$[O_3]_g = ([O_3]_{in} - [O_3]_{out})/\ln([O_3]_{in}/[O_3]_{out}). \quad (13)$$

The data presented in Fig. 2 show that in a wide interval of concentrations of different substrates ($[B]_0 \approx 10^{-4}$—10^{-3} mol L^{-1}) the absorption rate $\bar{V}$ is independent of the substrate concentration. This indicates that the reaction is controlled by mass transfer and the process occurs in the diffusion region. In this case, the interface surface (*a*) can be determined by Eq. (6).

The absorption rate $\bar{V}$ increases ($[B]_0 > 5 \cdot 10^{-3}$ mol L^{-1}) with an increase in $[B]_0$. In the framework of the film theory, this indicates a change in the reaction regime.[3] In this concentration interval the reaction occurs predominantly in the film, which is indicated by the coefficient values $E > 1$ obtained by Eq. (7) (see Table 1). The *Ha* number and the *k* reaction constant were determined from the *E* coefficient values by Eqs (8) and (9). The *E* coefficients, *Ha* numbers, and reaction rate constants for phenol, veratrole, veratric aldehyde, and veratric alcohol are given in Table 1.

As can be seen from the data in Table 1, the reaction rates determined at different substrate concentrations

Table 1. Kinetic parameters in the reactions of ozone with the model compounds calculated from the experimental data on ozone absorption

Substrate	$[B]_0$/mol L^{-1}	V/mol L^{-1} s^{-1}	E	E_i	Ha	k/L mol^{-1} s^{-1}
Phenol	$2.9 \cdot 10^{-4}$	$1.0 \cdot 10^{-6}$	1.00	1.37	—	—
	$5.8 \cdot 10^{-4}$	$1.0 \cdot 10^{-6}$	1.00	1.74	—	—
	$2.1 \cdot 10^{-3}$	$1.0 \cdot 10^{-6}$	0.95	3.53	—	—
	$2.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-7}$	1.00	3.86	—	—
	$2.0 \cdot 10^{-2}$	$1.7 \cdot 10^{-6}$	1.73	29.3	1.62	$5.8 \cdot 10^{3}$
	$3.4 \cdot 10^{-2}$	$2.0 \cdot 10^{-6}$	2.09	49.4	2.04	$5.5 \cdot 10^{3}$
	$4.1 \cdot 10^{-2}$	$2.5 \cdot 10^{-6}$	2.41	53.9	2.40	$6.3 \cdot 10^{3}$
	$5.3 \cdot 10^{-2}$	$2.7 \cdot 10^{-6}$	2.92	76.0	2.94	$7.4 \cdot 10^{3}$
Veratrole	$1.1 \cdot 10^{-5}$	$4.1 \cdot 10^{-7}$	0.34	1.02	—	—
	$3.5 \cdot 10^{-5}$	$6.1 \cdot 10^{-7}$	0.50	1.05	—	—
	$1.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-6}$	1.00	1.27	—	—
	$5.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-6}$	1.00	1.82	—	—
	$1.0 \cdot 10^{-3}$	$1.2 \cdot 10^{-6}$	0.99	2.59	—	—
	$1.3 \cdot 10^{-2}$	$2.6 \cdot 10^{-6}$	2.19	21.8	2.19	$1.6 \cdot 10^{4}$
	$2.5 \cdot 10^{-2}$	$4.2 \cdot 10^{-6}$	3.02	35.1	3.10	$1.7 \cdot 10^{4}$
	$3.8 \cdot 10^{-2}$	$3.7 \cdot 10^{-6}$	3.23	64.0	3.28	$1.3 \cdot 10^{4}$
Veratric alcohol	$3.1 \cdot 10^{-4}$	$7.1 \cdot 10^{-7}$	0.53	1.42	—	—
	$3.8 \cdot 10^{-4}$	$1.0 \cdot 10^{-6}$	0.72	1.48	—	—
	$5.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-6}$	0.97	1.71	—	—
	$1.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-6}$	1.04	2.87	—	—
	$4.4 \cdot 10^{-3}$	$2.2 \cdot 10^{-6}$	1.67	6.87	1.61	$2.7 \cdot 10^{4}$
	$1.2 \cdot 10^{-2}$	$4.0 \cdot 10^{-6}$	3.16	18.1	3.37	$4.4 \cdot 10^{4}$
Veratric aldehyde	$3.6 \cdot 10^{-5}$	$2.0 \cdot 10^{-7}$	0.18	1.05	—	—
	$3.6 \cdot 10^{-4}$	$9.8 \cdot 10^{-7}$	0.93	1.46	—	—
	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-6}$	1.01	2.37	—	—
	$2.7 \cdot 10^{-3}$	$1.1 \cdot 10^{-6}$	1.00	4.37	—	—
	$7.6 \cdot 10^{-3}$	$1.3 \cdot 10^{-6}$	1.22	10.7	0.85	$4.3 \cdot 10^{3}$
	$1.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-6}$	1.45	25.5	1.23	$3.8 \cdot 10^{3}$

agree satisfactorily between each other. The experimental data are well described by the theoretical curve (Fig. 3), which shows the dependence of the ozone absorption rate on the phenol concentration in different reaction regimes. This dependence was calculated by Eqs (7)—(13) and indicates the correct choice of the kinetic equations describing the reaction of ozone with phenol. Similar dependences were obtained for veratrole and its derivatives.

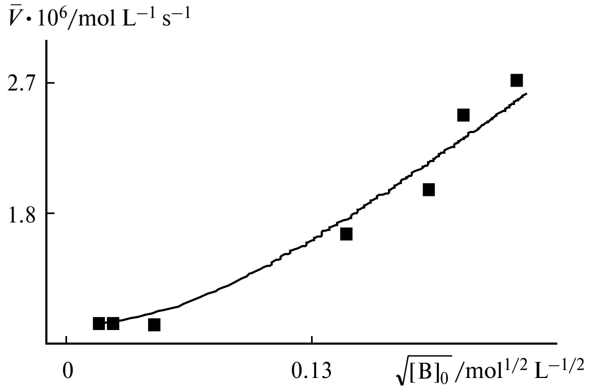

Fig. 3. Experimental (points) and theoretical (line) plots of $\bar{V}$ *vs* $\sqrt{[B]_0}$ for phenol.

The reaction rate constant was determined by both ozone absorption and a change in the substrate concentration. The plots of the concentrations of phenol, veratrole, and veratric alcohol *vs* ozonization duration are presented in Figs 4, *a—c*.

In the case when absorbed ozone reacts completely with an organic substance, the ozone absorption rate is equal to the rate of substrate consumption. For the reaction

$$z\,O_3 + B \longrightarrow P$$

we can write

$$\bar{V} = z(-d[B]/dt), \qquad (14)$$

where z is the ozone consumption (number of moles of ozone consumed for the oxidation of 1 mole of substrate, and ozone is consumed for the oxidation of the substrate and intermediate ozonization products), and [B] is the substrate concentration at the moment t.

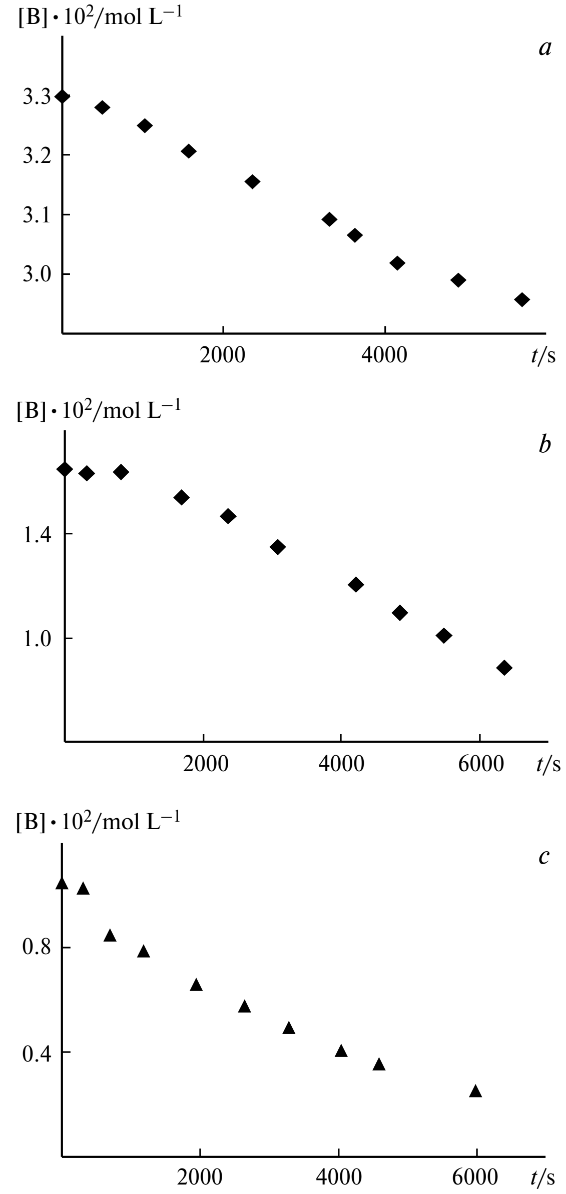

Fig. 4. Kinetics of changing the concentration of phenol (*a*), veratrole (*b*), and veratric alcohol (*c*) *vs* ozonization time.

For the reactions in the film, one can determine the reaction rate constant by a change in the substrate concentration during ozonization.[14] Substituting Eqs (7) and (9) into formula (14), we have

$$\bar{V} = z(-\mathrm{d}[\mathrm{B}]/\mathrm{d}t) = [\mathrm{O}_3]^* a\sqrt{D_{\mathrm{O}_3} k[\mathrm{B}]}. \quad (15)$$

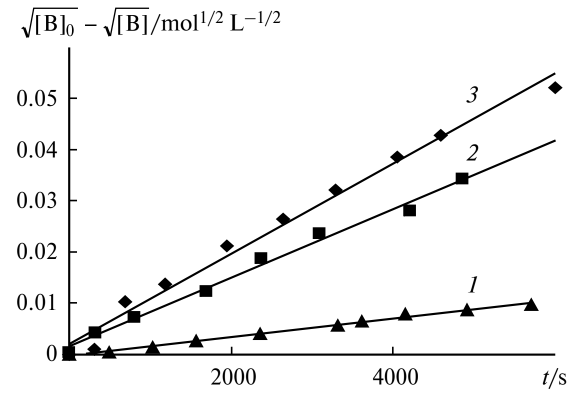

Fig. 5. Plots of $\sqrt{[\mathrm{B}]_0} - \sqrt{[\mathrm{B}]}$ *vs* ozonization time for phenol (*1*), veratrole (*2*), and veratric alcohol (*3*) (initial concentrations $3.3 \cdot 10^{-2}$, $1.6 \cdot 10^{-2}$, and $1.1 \cdot 10^{-2}$ mol L^{-1}, respectively).

After integration Eq. (15) takes the form

$$\sqrt{[\mathrm{B}]_0} - \sqrt{[\mathrm{B}]} = k' t, \quad (16)$$

where $k' = [a[\mathrm{O}_3]^*/(2z)]\sqrt{D_{\mathrm{O}_3} k}$, and $[\mathrm{B}]_0$ is the initial substrate concentration.

The experimental data in the coordinates of Eq. (16) for phenol, veratrole, and veratric alcohol are presented in Fig. 5. Using these data, the k' value was determined for various substrates.

To calculate the rate constant, one should know the value

$$z = (\Delta[\mathrm{O}_3]_t)/(\Delta[\mathrm{B}]_t), \quad (17)$$

where $\Delta[\mathrm{O}_3]_t$ is the amount of ozone absorbed to the moment t, which is determined from the kinetic curves (see Fig. 1); $\Delta[\mathrm{B}]_t$ is the amount of the substrate oxidized to the moment t determined from the kinetic curves (see Fig. 4). An analysis of the experimental data showed that the z value remains virtually unchanged during the reaction.

The ozonization rate constants determined from the change in the substrate concentration for phenol, veratrole, and veratric alcohol are listed in Table 2.

The data in Tables 1 and 2 show that the rate constants of the processes under study determined by various methods agree well between each other.

The kinetics of phenol ozonization has been studied in detail.[8,9,15,16] However, a comparison of the known

Table 2. Rate constants for the reactions of ozone with model compounds calculated from the chromatographic data

Substrate	$[\mathrm{B}]_0 \cdot 10^2$/mol L^{-1}	*E*	*Ha*	*z*	$k' \cdot 10^6$/mol$^{0.5}$ L$^{-0.5}$ s^{-1}	$k \cdot 10^{-4}$/L mol^{-1} s^{-1}
Phenol	3.3	2.18	2.14	3.1	1.8	0.57
Veratrole	1.6	2.30	2.34	2.3	5.6	1.5
Veratric alcohol	1.1	2.89	3.04	2.5	8.0	4.4

rate constant values for this reaction is rather difficult. This is related first of all to different experimental conditions and specific features of the methods used for the calculation of the kinetic parameters. Therefore, the earlier[8,9,15,16] published values for the rate constants differ strongly: from $1.0 \cdot 10^3$ to $3.5 \cdot 10^4$ L mol^{-1} s^{-1}.

Data on the kinetics of the reactions of compounds modeling the structural fragments of lignin (for instance, guaiacol, veratrole, and their derivatives) with ozone are virtually lacking. Therefore, in the present work we attempted to estimate the rate constants for the ozonization of veratrole and its derivatives under the same experimental conditions, namely, when the reactions occur in the film. This made it possible to compare the reactivity of these compounds in the reaction with ozone.

Based on the results obtained, we can conclude that the nature of substituents in the aromatic ring of veratrole affects the reactivity of the compounds under study. The presence of electron-releasing substituents in the aromatic ring increases the reactivity, whereas for electron-withdrawing substituents the reactivity decreases appreciably, which is indicated by the rate constant values for the ozonization of model lignin compounds (see Tables 1 and 2).

References

1. K. V. Sarkanen and I. Lyudvig, *Ligniny — struktura, sostav i reaktsii* [*Lignins: Structure, Composition, and Reactions*], Lesnaya Promyshlennost´, Moscow, 1975, 613 pp. (in Russian).
2. P. S. Bailey, *Ozonization in Organic Chemistry*, Academic Press, New York, 1982, Vol. **2**, 31 p.
3. P. V. Danckwerts, *Gas-Liquid Reactions*, McGrow-Hill Book Company, New York, 1970, 256 pp.
4. H. Benbelkacem and H. Debellefontaine, *Chem. Eng. Proc.*, 2003, **42**, 723.
5. M. M. Ksenofontova, A. N. Mitrofanova, E. A. Tveritinova, A. N. Pryakhin, and V. V. Lunin, *Zh. Fiz. Khim.*, 2003, **77**, 1028 [*Russ. J. Phys. Chem.*, 2003, **77**, No. 6 (Engl. Transl.)].
6. A. D. Mitrofanov, Deposited with ONIITEKhIM, Cherkassy, 1979, Ferbuary 5, No. 2363-79 (in Russian).
7. V. N. Sokolov and I. V. Domanskii, *Gazozhidkostnye reaktory* [*Gas-Liquid Reactors*], Mashinostroenie, Leningrad, 1976, 216 pp. (in Russian).
8. V. A. Yakobi, *Zh. Fiz. Khim.*, 1992, **66**, 867 [*Russ. J. Phys. Chem.*, 1992, **66**, No. 4 (Engl. Transl.)].
9. G. A. Galstyan, N. F. Tyupalo, and S. D. Razumovskii, *Ozon i ego reaktsii s aromaticheskimi soedineniyami v zhidkoi faze* [*Ozone and Its Reactions with Aromatic Compounds in the Liquid Phase*], Eastern-Ukrainian National University, Lugansk, 2003, 298 (in Russian).
10. W. J. Masschelein, *Ozone Science Eng.*, 1998, **20**, 491.
11. F. J. Beltran, J. F. Garcia-Araya, and J. M. Encinar, *Ozone Science Eng.*, 1997, **19**, 281.
12. H. Benbelkacem, H. Cano, S. Mathe, and H. Debellefontaine, *Ozone Science Eng.*, 2003, **25**, 18.
13. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill Book Gompany, New York, 1987, 741 pp.
14. J. Beltran-Heredia and J. Torregrosa, *Wat. Res.*, 2001, **35**, 1077.
15. J. Hoigne and H. Bader, *Wat. Res.*, 1983, **17**, 185.
16. P. C. Singer and M. D. Gurol, *Wat. Res.*, 1983, **17**, 1163.

Received May 22, 2007;
in revised form July 31, 2007