Dynamics of the reaction of ozone with humic and fulvic acids in lake water, and the structures of fragments of their molecules

S. D. Razumovskii, V. V. Podmaster'ev, and M. L. Konstantinova*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

The rates of ozone absorption during bubbling of an ozone—oxygen mixture through a sample of lake water with high contents of humic and fulvic acids were measured. Three characteristic sections were distinguished on the kinetic curve. The corresponding effective rate constants of ozone reactions with the substrate are $5.1 \cdot 10^4$, $1.4 \cdot 10^2$, and 7.6 L mol^{-1} s^{-1}. Structures of the reacting fragments and their contents in the system were suggested.

Key words: humic acids, fulvic acids; ozone.

Products of biochemical degradation of plant residues, namely, humic acids (HA) and fulvic acids (FA), are known to be the main components of natural surface water, FA being the major component (normally >80 %).[1–3] Humic and fulvic acids play an important role in natural processes. In particular, they form stable complexes with Co^{2+}, Mg^{2+}, Fe^{n+}, and other cations and thus transport them for long distances in the ground or on the surface.[4] It is supposed that they can serve as carriers for radionuclides[3,5] and noble metals.[6]

In processes of water treatment in which chlorine is used for sterilization, halomethanes and many other toxic compounds are formed from HA and FA. Removal or destruction of humic and fulvic acids prior to chlorination of water could lead to a decrease in the consumption of chlorine and a decrease in the proportion of halomethanes in the drinking water leaving the water treatment system.[7] This accounts for the interest in the investigation of the properties and structures of HA and FA. At present, too little is known about these compounds. A variety of investigation procedures made it possible to obtain extensive information concerning the major components of HA and FA, but at the same time, some inconsistencies arose in the interpretation of the results.[8]

One of the successful approaches to understanding of the characteristic features of the HA and FA structures is the study of reactions peculiar to these compounds. Participation in azo coupling, together with characteristic bands in the IR spectra indicate the presence of aromatic rings in the molecules;[1,9] acidic properties of hydroxyl groups point to the presence of phenol fragments;[3] the tendency to form salts means that the molecules contain carboxylic groups, *etc.*

Study of the kinetics of reactions of HA and FA also seems promising. Structural fragments of most of organic compounds retain their individual natures to a large degree, and their participation in some specific reactions as well as characteristic features of the kinetics of these reactions provide information concerning these fragments and their environment.[11]

The results of our study of the dynamics of the ozone reaction with samples of natural water containing large proportions of HA and FA are presented below.

Experimental

Lake water containing large proportions of plant and peat degradation products was used as the object of investigation. The water had the following characteristics: a color index against the cobalt-platinum scale of 400°; a weak marsh odor; a chemical oxygen demand (COD) of 380 mg L^{-1}; a content of suspended particles of 1.2 mg L^{-1}; pH 6.6.

Ozone was obtained by passing oxygen through an electric discharge area (v_g = 1.67 mL s^{-1}). The concentrations of ozone at the inlet and the outlet of the reactor were measured by spectrophotometry based on the absorption at λ = 300 nm. The dynamics of ozone reaction with organic components of water was studied in a unit, whose scheme is shown in Fig. 1. A flow of ozone-oxygen mixture was bubbled through 150—500 mL of water placed in a glass bubble reactor having a porous disperser at the bottom and a pipe leading to an optical cell at the top. The concentrations of ozone at the inlet and the outlet of the reactor ($[O_3]_0$ and $[O_3]_g$) were determined at λ = 300 nm. The procedure of the measurement has been described in more detail previously.[11]

As the reaction proceeded, water samples were withdrawn for determining the color index and COD, based on the optical density at λ = 254 nm.

Results and Discussion

In the initial period of bubbling an ozone—oxygen mixture through the bulk of the water studied, ozone is

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 60—63, January, 1996.

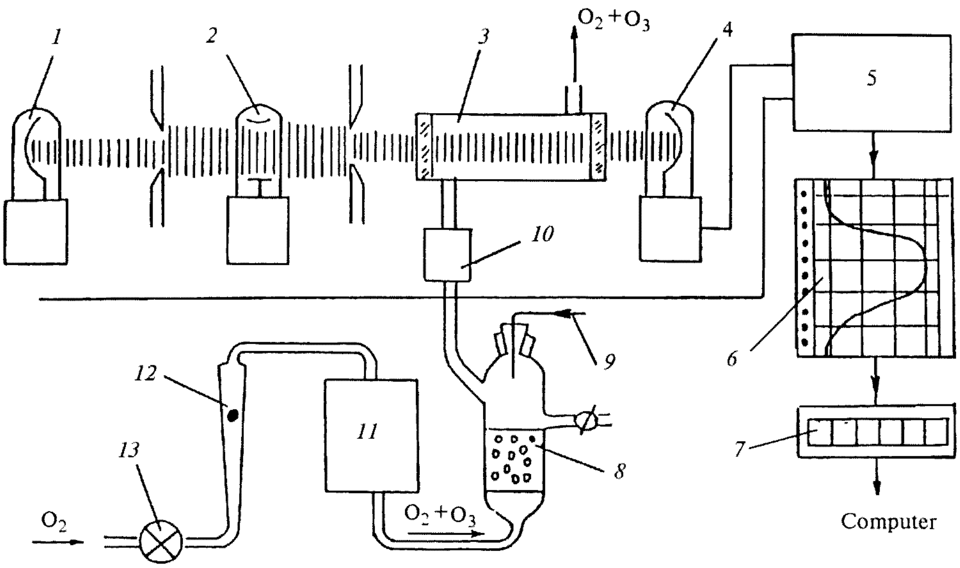


Fig. 1. Scheme of the experimental unit used to study the dynamics of the ozone reaction with HA and FA in water: *1*, cylinder with O_2; *2*, pressure regulator; *3*, rotameter; *4*, ozone generator; *5*, reactor; *6* and *7*, photoelectric cells; *8*, diaphragm; *9*, measuring cell; *10* and *11*, light guides; *12*, signal receiver; *13*, automatic recorder.

absorbed almost completely, which indicates that there are no diffusion restrictions for the reaction. Over subsequent time intervals, ozone is no longer completely absorbed, its amount passing through the water gradually increasing to its concentration at the inlet of the reactor. The results of one of the experiments are shown in Fig. 2. Since each run requires a prolonged period (>5 h), the initial section of the plot is presented in an extended time scale (curves *1* and *2*) with respect to the rest of the plot (curves *3* and *4*).

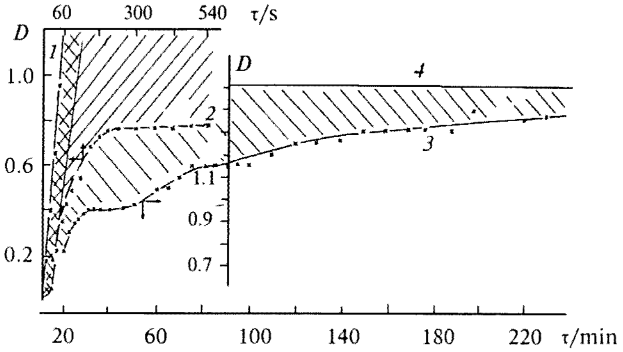


Fig. 2. Dependence of the optical density of ozone in the gas phase over the reactor on the duration of the ozone reaction with the sample of natural water: kinetics of the saturation of pure water with ozone (*1*); $[O_3]_g = f(\tau)$ dependence in an extended time scale (*2*); $[O_3]_g = f(\tau)$ plot in a compressed time scale (*3*); $[O_3]_0 = f(\tau)$ plot (*4*). V_l = 150 mL; υ_g = 1.67 mL s^{-1}; *D* is the optical density of the gas flow (*D* = 1 corresponds to $8.8 \cdot 10^{-4}$ mol L^{-1} $[O_3]$).

The difference between the $[O_3]_0$ and $[O_3]_g$ values at every instant characterizes the rate of the process (*w*) in this point

$$w = \omega([O_3]_0 - [O_3]_g), \qquad (1)$$

where ω/s^{-1} is the specific rate at which the gas is mixed with the liquid:

$$\omega = \upsilon_g/V_l = 1.67/150 = 1.1 \cdot 10^{-2},$$

and V_l is the volume of the liquid.

An examination of the character of the $[O_3]_g = f(\tau)$ plot indicates that the curve exhibits two clearly defined jumps, one of which appears 30 s after the beginning of the reaction, and the other is exhibited 20 min after the beginning of the reaction. The inflections correspond to points where reactive functional groups are completely consumed. The surface areas over these curves, enclosed by the $[O_3]_0$ line above, by the $[O_3]_g$ line below, and by conventional lines reflecting the rate of saturation of the solution with ozone in the absence of organic admixtures (line *1*) at the right and at the left, are equivalent to the amounts of the corresponding groups in the water under study. If we express the concentrations of these groups in mol-equiv. (analogously to the generally used determination of the contents of hardness salts in water), calculation makes it possible to find the concentrations of the corresponding fractions I—III (in mol-equiv. dm^{-3}): $[F^I] = 6 \cdot 10^{-6}$, $[F^{II}] = 4.5 \cdot 10^{-5}$, and $[F^{III}] = 4.13 \cdot 10^{-4}$.

To characterize these fractions more extensively, we evaluated their reactivities with respect to ozone; the effective rate constant (k_{eff}) of the reaction of the particular fraction with ozone served as the quantitative measure of its reactivity.

The results of our previous experiment[11] as well as results of other authors[12] indicate that reactions of ozone with organic impurities closely obey the bimolecular kinetics.

$$w = k_{\text{eff}}[\text{O}_3]_l[\text{F}], \qquad (2)$$

where [F] is the concentration of the corresponding fraction expressed in mol-equiv. of O_3.

By combining Eqs. (1) and (2), we obtain

$$k_{\text{eff}} = \frac{\omega([\text{O}_3]_0 - [\text{O}_3]_g)}{[\text{O}_3]_l[\text{F}]}.$$

Here we assume that under the conditions of our experiments, equilibrium ozone concentrations in the solutions are achieved, *i.e.*,

$$[\text{O}_3]_l = \alpha[\text{O}_3]_g,$$

where $\alpha = 0.27$ is the Henry coefficient obtained in the preliminary runs; $[O_3]$ is proportional to the experimentally determined optical density (D).

For fraction III, the calculation yields

$$k_{\text{eff}}^{\text{III}} = 1.1 \cdot 10^{-2} \frac{1.5 - 1.0}{0.27 \cdot 1.0 \cdot 2.75 \cdot 10^{-3}} = 7.6 \text{ L mol}^{-1} \text{ s}^{-1}.$$

In the calculation of $k_{\text{eff}}^{\text{II}}$ we took into account the fact that the absorption of ozone by the system consists of two parts, namely, oxidation of fraction III and reaction with fraction II:

$$w = \omega([\text{O}_3]_0 - [\text{O}_3]_g) - k_{\text{eff}}^{\text{III}}[\text{F}^{\text{III}}][\text{O}_3]_g,$$

from which it follows that

$$k_{\text{eff}}^{\text{II}} = \frac{1.1 \cdot 10^{-2}(D_0 - D_g) - 2.1 \cdot 10^{-2} \cdot 2.75 \cdot 10^{-3} \cdot D_g}{0.27 \cdot 3 \cdot 10^{-4} \cdot D_g} = 1.4 \cdot 10^2 \text{ L mol}^{-1} \text{ s}^{-1}.$$

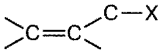
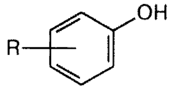
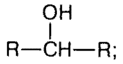
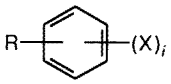
To calculate $k_{\text{eff}}^{\text{I}}$, we should subtract the rates of ozone reactions with F^{II} and F^{III} from the overall rate of the consumption of ozone.

$$k_{\text{eff}}^{\text{I}} = \frac{\omega(D_0 - D_g) - k_{\text{eff}}^{\text{III}}[\text{F}^{\text{III}}] - k_{\text{eff}}^{\text{II}}[\text{F}^{\text{II}}]}{\alpha[\text{F}^{\text{I}}]D_g}$$

In this case, the contributions of $[F^{III}]$ and $[F^{II}]$ proved to be small, therefore to sufficient accuracy, we may obtain

$$k_{\text{eff}}^{\text{I}} = \frac{1.1 \cdot 10^{-2} \cdot 1.5}{0.27 \cdot 4 \cdot 10^{-5} \cdot 0.13} = 5.1 \cdot 10^4 \text{ L mol}^{-1} \text{ s}^{-1}.$$

Table 1. Suggested structures for fractions I, II, III, and IV in fulvic acids that correspond to the found values of the rate constants of the reactions

Fraction	k_{eff}^i /L mol^{-1} s^{-1}	Molar fraction (%)	Assumed structure of the fragment
I	$5 \cdot 10^4$	1.2	
II	$1.4 \cdot 10^2$	9.6	
III	7.6	89	 $R{-}\overset{\text{OH}}{\text{CH}}{-}R$; R—CH$_2$—OH
IV	<0.1	Not estimated	 or —(—CH$_2$—)$_n$—

Note. X is an electronegative substituent (carbonyl, carboxyl, or hydroxyl).

The numerical values of the effective rate constants, together with the published data on the composition of FA (C, 38—40; H, 3.9—4.2; O, 56—58 %), their molecular weights (~300—600), and the contents of carboxylic (2—3 mg-equiv. per g) and carbonyl groups (6.3—8.3 mg-equiv. per g)[1,7,8] allow one to make some inferences concerning the structure of the fragments of fulvic acids.

Functional groups of complex organic compounds incorporated into molecules of various structures often retain their individual features. In particular, this refers to their reactivities with respect to ozone. An analysis of the array of kinetic data[5] makes it possible to assign the $k_{\text{eff}}^{\text{I}}$, $k_{\text{eff}}^{\text{II}}$, and $k_{\text{eff}}^{\text{III}}$ values to the probable structures of the reactive fragments of fulvic acids (Table 1).

The interpretation of the structures of fractions I and II is apparently sufficiently reliable, since the values of the effective rate constants of their reactions do not overlap with those of the reactions of other structural fragments of the acids. The structure of fraction III is somewhat more difficult to determine: Table 1 contains two structures, whose presence is beyond doubt. In addition, the products of the first and second steps also fall into the region of the reaction of fraction III, and this should also be taken into account in the discussion (by decreasing the concentration of fraction III in favor of fraction II). The presence of fraction IV is confirmed by the existence of an organic residue that is difficult to oxidize (~20 %) in the system, as shown by other methods.

The results of parallel studies of FA by pyrolytic GC/MS[8] indicate that the 230 compounds identified can be grouped in two classes: those containing phenoxyl and phenyl(mono-, di-, and tri-)carboxyl fragments. This is in good agreement with the data of Table 1.

An advantage of the study of the dynamics of ozone reaction with HA and FA in water is that the number of procedures affecting the acids is small. This allows one to hope that the primary structures found from this study are close to the natural structures of these compounds.

References

1. G. M. Varshall, in *Problemy analiticheskoi khimii*, **V**, *Metody analiza prirodnykh vod* [*Problems of Analytical Chemistry*, **V**, *Methods of Analysis of Natural Water*], Nauka, Moscow, 1977, 94 (in Russian).
2. V. D. Grebenyuk, N. P. Strizhak, G. V. Slavinskaya, G. V. Lantukh, G. M. Popovich, V. V. Goncharuk, A. V. Grechko, and A. O. Samsoni-Todorov, *Khim. Tekhnol. Vody* [*Chemistry and Technology of Water*], 1989, **11**, 804 (in Russian).
3. J. I. Kim, G. Buckau, G. H. Li, H. Duschner, and N. Psaros, *Fresenius J. Anal. Chem.*, 1990, **338**, 245.
4. G. Sposito, *CRS Crit. Rev. Environ. Control*, 1986, **16**, 193.
5. D. B. Kent, V. S. Tripathi, N. B. Ball, and J. O. Leckie, *US Nucl. Reg. Comm. NUREG Rept.*, CR-4897.
6. S. A. Wood, C. D. Tait, D. Vlassopoulos, and D. R. Janecky, *Geochim. Cosmochim. Acta*, 1994, **58**, 625.
7. S. G. Konsushko, G. G. Rudenko, M. A. Chaikovskaya, and N. A. Sinel'nik, *Gor. Khoz. Ukr.* [*Municipal Services in Ukraine*], 1985, No. 1, 26 (in Russian).
8. C. Salz-Jimenez, *Environ. Sci. Technol.*, 1994, **28**, 197.
9. M. Schnitzer and S. U. Khan, *Humic Substances in the Environment*, Marcel Dekker, New York, 1972.
10. F. J. Stevenson, *Humus Chemistry, Genesis, Composition, Reactions*, Wiley, New York, 1982.
11. S. D. Razumovskii and G. E. Zaikov, *Ozon i ego reaktsii s organicheskimi soedineniyami* [*Ozone and Its Reactions with Organic Compounds*], Nauka, Moscow, 1974 (in Russian).
12. J. Hoigne and H. Bader, *Water Res.*, 1983, **17**, 173.

Received March 3, 1995;
in revised form June 22, 1995