Decomposition of Aqueous Diphenyloxide by Ozonolysis and by Combined γ-Ray-Ozone Processing

Petar Popov and Nikola Getoff*

Ludwig Boltzmann Institute for Radiation Chemistry and Radiation Biology,
c/o The University of Vienna, Althanstr. 14, A-1090 Wien, Austria. Fax: ++43-1-4277 52795.
E-mail: nikola.getoff@univie.ac.at

* Author for correspondence and reprint requests

Z. Naturforsch. **59 c**, 146–150 (2004); received March 31/May 20, 2003

Diphenyloxide (DPO) is one of many, rather toxic pollutants produced by combustion of fossil fuels, which are emitted to the atmosphere with flue gases and brought to ground water by rain and snow. Its decomposition is investigated by ozonolysis at room temperature and the major products like phenol, resorcinol, hydroquinone, dihydroxy-benzoic acid as well as the total yield of aldehydes and carboxylic acids were determined as a function of applied ozone concentration. In addition, the DPO-degradation was studied by a combined action of γ-ray under continuous bubbling of a known ozone concentration. In this case the formation of the same products is observed, but their yields differ from the above ones. Based on the synergistic action of ozone and γ-ray the DPO-radiolysis is rather efficient, leading to an initial-G-value of 11.3. Some probable reaction mechanisms are presented for explanation of the degradation process.

Key words: Diphenyloxide, Ozonolysis, γ-Ray-Ozone Processing

Introduction

By combustion of coal in the caloric electrical plants, steel industry etc. in addition to NO_x, SO_2/SO_3 (acid rain precursors) also a number of rather toxic polycyclic aromatic hydrocarbons, such as diphenyloxide, fluorene, fluoranthene, naphthalene, anthracene, benzo[a]pyrene are formed. They are emitted with the flue gases into the atmosphere and by rain and snow they can be brought to the ground water. These substances are carcinogenic, even in very small concentration, namely from 3×10^{-2} (diphenyloxide) to 1×10^{-6} (benz[a]pyrene) mg/m^3 flue gas. Moreover, these pollutants are strongly involved in the ozone depletion of the atmosphere.

The present study deals with the degradation of diphenyloxide (DPO) in aqueous solution, taken as a model for this group of compounds. Two procedures were selected for this purpose: ozonolysis and combined γ-ray-ozone treatment. Ozone is known as a powerful oxidizing agent and therefore is also used on a technical scale for water purification (Masscheln, 1982; Rice and Netzer, 1984; Hoigne, 1998). Besides, the synergistic effect of ozone combined with γ-ray, electron beam, UV-light and TiO_2-catalyst was also studied in various systems (*e.g.* Aray *et al.*, 1986; Getoff, 1992; Gehringer *et al.*, 1992; Getoff, 1993; Krapfenbauer and Getoff, 1999; Winarno and Getoff, 2002; Sanchez *et al.*, 2002).

Experimental

Aqueous solutions (pH 10–10.5) of diphenyloxide (DPO), $(C_6H_5)_2O$, purity $\geq$ 98% (Fluka), were freshly prepared using triple distilled water. The solubility of DPO in water is rather low, hence its concentration was controlled by measuring the absorption spectrum (Perkin Elmer UV/VIS LAMBDA 16 spectrophotometer) at λ_{max} = 270 nm, $\varepsilon_{270} = 2230\,l \cdot mol^{-1} \cdot cm^{-1}$. Substrate concentrations of 5×10^{-5} to 3×10^{-4} $mol \cdot l^{-1}$ were used throughout the experiments.

Ozone of the desired flow concentration (mg O_3/min) was supplied by OZAT CFS-1A, 3 A model (Ozonia Corp., Dübendorf, Switzerland). A Gammacell 220 (Nordion International Inc., Canada) provided a γ-rays dose rate of 70 Gy/min. The product analysis was carried out by HPLC (Hewlett-Packard, model 1046/1050) in combination with programmable detectors for fluorescence (HP1046), electrochemical measurements (HP1049) and absorption surveying (HP1100). Very good results were obtained using a Hypersil ODS column, 4.0 mm × 125 mm and a solvent mix-

0939–5075/2004/0100–0146 $ 06.00

ture of 30 vol.% H_2O and 70 vol.% methanol with a flow rate of 1 ml/min.

The yields of the major degradation products were determined by means of internal standards using HPLC. In addition a mixture of various aldehydes and carboxylic acids were also formed as DPO-degradation products. Their satisfactory separation and identification could not be achieved in this way. Hence, the formation and decomposition of the aldehydes were followed spectrophotometrically by using the 2,4-dinitrophenylhydrazine method (Getoff and Seitner, 1966). On the other hand the pH-decrease of the solution as a function of the applied ozone quantity was taken as a measure for the formation of carboxylic acids.

The aim of the present study was to compare the degradation of DPO by the above mentioned two procedures: ozonolysis and combined γ-ray-ozone processing.

Results and Discussion

Ozonolysis of DPO

Several series of experiments were carried out by gassing the DPO-solution with different ozone concentrations at room temperature in special glass vessels (20 ml solution). At given treatment times aliquots were taken for analysis. Fig. 1 shows the degradation of 2×10^{-4} mol/l DPO as a function of applied ozone. More than 60% of the pollutant is decomposed by consumption of about 0.25 mg O_3/ml at the beginning of the treatment (Fig. 1, curve A). Subsequently the degradation reaction proceeds rather slowly. Obviously, the resulting products undergo a further degradation by using up ozone.

The yields of the observed major products are likewise given as a function of ozone consumption as insert in Fig. 1. Phenol (curve B) and dihydroxybenzoic acid (curve E) appear to be the main products. Resorcinol (curve C) and hydroquinone (curve D) very likely seem to originate by hydroxylation of phenol. This process is previously reported by γ-ray degradation of aqueous phenol (Getoff, 1986). It is interesting to point out that, while the formation of pyrocatechol, appearing as one of the major products of phenol degradation by γ-ray in the presence of air (Getoff, 1996), only traces of it were observed in the present study.

As further degradation products, resulting by ozonolysis of aqueous DPO a mixture of aldehydes and carboxylic acids was observed by HPLC. However, they could not be satisfactory separated and identified. Hence, their relative yields are presented in Fig. 2 as a function of applied ozone. The pH-decrease representing the produced carboxylic acids in the treated solutions is rather strong up to the consumption of about one mg O_3/ml and after that levels off (Fig. 2, curve A). The course of the curve is similar to that of curve A, Fig. 1, showing the DPO-ozonolysis.

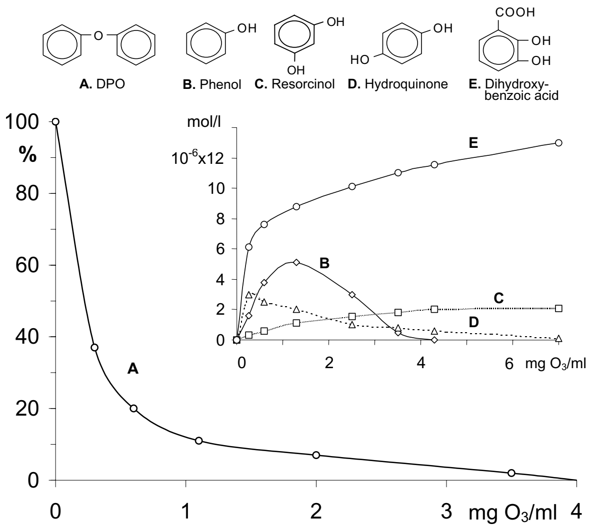

Fig. 1. Degradation of aqueous 2×10^{-4} mol/l diphenyloxide (DPO) by ozone-treatment at pH 10; $[O_3]$ = 0.35 mg/ml · min.
Insert: Formation of major degradation products resulting of the ozone treatment.

The mixture of aldehydes, measured as 2,4-dinitrophenylhydrazone, is presented as OD-values (1 cm light path) in dependence on the applied mg

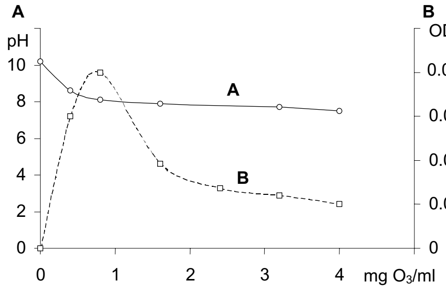

Fig. 2. Formation of carboxylic acids (expressed as pH-change), (A), and aldehydes (measured as 2,4-dinitrophenylhydrazone), (B), resulting from degradation of aqueous 10^{-4} mol/l DPO (pH 10.2) under a continuous flow of 0.2 mg O_3/min.

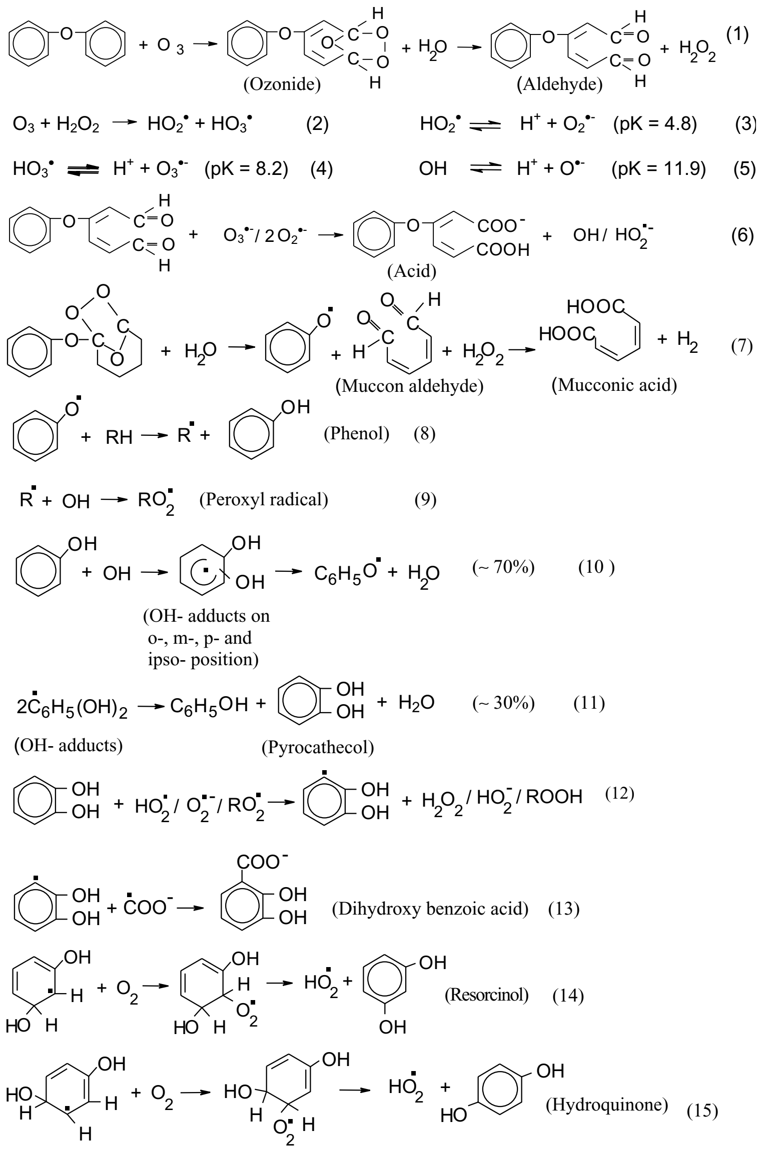

Fig. 3. Some possible reactions involved in the ozonolysis of diphenyloxide.

O_3/ml (Fig. 2, curve B). It shows a strong similarity to the phenol formation (see curve B, Fig. 1). The aldehydes are oxidized further to carboxylic acids and other compounds; therefore their yield is rather low.

Based on the obtained experimental results it can be stated that aqueous DPO can be successfully decomposed by ozone. In alkaline aqueous solution at room temperature ozone is not stable. It decomposes according to a chain-reaction, leading to the formation of several oxidizing radicals: OH, $HO_2^{\bullet}/O_2^{\bullet}$, $HO_3^{\bullet}$, $HO_2^{\bullet}$ etc. as well as H_2O_2 (Getoff, 1997, and ref. therein). Each of these species can attack the substrate and initiate its degradation. It might be also mentioned that the first step of ozone reaction with olefins and aromatic compounds can be designated as an electrophilic addition process on the double bonds with the formation of the corresponding unstable ozonide. The ozonide usually undergoes hydrolysis initiating a stepwise degradation of the pollutant. Some possible major reactions are presented in Fig. 3 for illustration of DPO-ozonolysis in aqueous basic solution.

O_3 as well as the other oxidizing species mentioned above can attack the double bonds of the DPO-molecule on different positions leading to the formation of various transients. The last ones are subsequently oxidized to aldehydes and carboxylic acids and finally to CO_2 and H_2O. These reaction steps are not further discussed.

Combined γ-ray-ozone processing of DPO

Water radiolysis

For completeness of the subject matter the radiolysis of the water is briefly mentioned. The processes resulting by absorption of ionizing radiation in water are comprised in Fig. 4. The primary products and water radiolysis as well as their yields (G_i-values) in the pH range of 5 to 8.5 are also presented. With increasing the pH value of the solution the H-atoms are converted to e^-_{aq} ($H + OH^- \rightarrow e^-_{aq}$, $k = 2.5 \times 10^7\ l \cdot mol^{-1} \cdot s^{-1}$; see *e.g.* Getoff, 1996), but the total yield of the reducing species remains the same. On the other hand in strong basic solutions the OH radicals dissociate to $O^{\cdot-}$ species (pK = 11.9; see also Fig. 3), which have, however, somewhat different reactivity.

DPO degradation by combined action of γ-ray and ozone

As mentioned above by simultaneous action of γ-ray and ozone a strong synergistic effect has been established on the degradation of various water pollutants (*e.g.* Getoff, 1992, 1993, 1996, 1997, 1999, 2001; Getoff and Solar, 1998; Gehringer *et al.*, 1992; Krapfenbauer and Getoff, 1999; Sanchez *et al.*, 2002; Winarno and Getoff, 2002). Based on these experiences and knowledge several series of experiments were now performed concerning the γ-ray induced degradation of DPO under permanent gassing of known ozone concentration in the solution. The course of the degradation process as well as of the resulting major products are presented in Fig. 5. Obviously under these conditions the DPO-decomposition is much more efficient as observed by ozonolysis only (compare curve A in Fig. 1 and 5). This fact reflects the action of various oxidizing radicals produced by the radiolysis of water as well of ozone, which are involved in the manifold oxidation process.

$$H_2O \rightsquigarrow H_2O^* \longrightarrow H + OH \quad (16)$$

$$\longrightarrow H_2O^+ + e^- \quad (17)$$

$$e^- \longrightarrow e^-_{th} + nH_2O \longrightarrow e^-_{aq} \text{ (solvated electron)} \quad (18)$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+(H^+_{aq}) + OH \quad (19)$$

$$e^-_{aq} + OH \longrightarrow OH^-_{aq} \quad (20)$$

$$e^-_{aq} + H^+_{aq} \longrightarrow H \quad (21)$$

Primary products of water radiolysis :

$$H_2O \rightsquigarrow e^-_{aq}\ ,\ H\ ,\ OH\ ,\ H_2\ ,\ H_2O_2\ ,\ H^+_{aq}\ ,\ OH^-_{aq} \quad (22)$$

$$G_i = (2.7)\ (0.6)\ (2.8)\ (0.45)\ (0.72)\ (3.2)\ (0.5)$$

Fig. 4. Water radiolysis and yields (G-values) of primary products in pH-range 5 to 8.5.
G-value = number of produced or decomposed species per 100 eV absorbed energy. G_i = initial G-value, calculated before secondary reactions start (see Getoff, 1996).

It is interesting to note, that in this case the yield of the produced mixture of aldehydes and carboxylic acids (Fig. 6) is much higher than their yield observed by ozonolysis only (see Fig. 2). This fact suggests that the oxidizing degradation of DPO is much more efficient by combined action of γ-ray and ozone. Hence, in addition to the reactions presented in Fig. 3 also the increased concentration

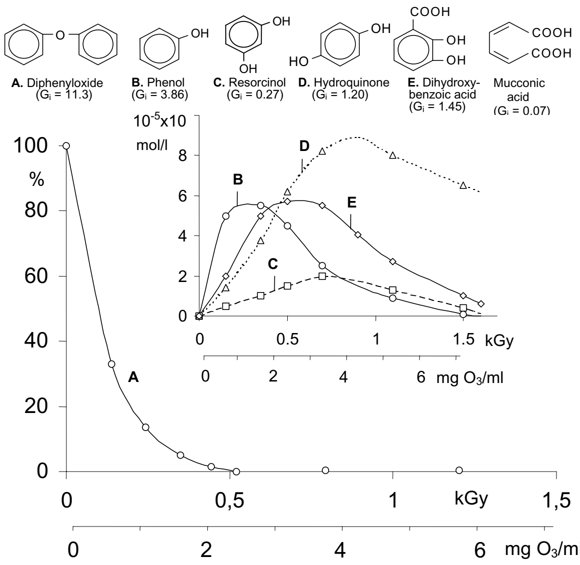

Fig. 5. Radiation-induced degradation of 2.4×10^{-4} mol/l diphenyloxide (A; DPO) at pH 10 by passing through 0.35 mg O_3/ml · min during the irradiation treatment with γ-ray as a function of dose (kGy).
Insert: Yield-dose curves of the major radiolytic products, their formula and observed initial-G-values (G_i). The curve of mucconic acid is not given in the insert.

of OH radical and various peroxyl radicals ($O_2^{\cdot -}$, $HO_3^{\cdot}$, $HO_4^{\cdot}$, $ROO^{\cdot}$ etc.) originating from the ozonolytic processes are playing a crucial role in the synergistic treatment of the pollutant.

The obtained results also demonstrate the consecutive formation of low molecular aldehydes and carboxylic acids, resulting from the aromatic products (see Fig. 5), formed at the beginning of the treatment. A prolonged combined treatment with γ-ray in the presence of ozone can cause a substrate degradation up to CO_2 and H_2O.

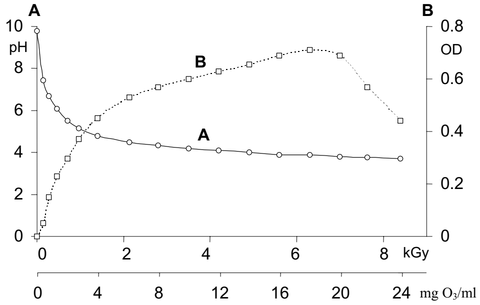

Fig. 6. Formation of carboxylic acids (expressed as pH-change), (A), and aldehydes (measured as 2,4-dinitrophenylhydrazone at 550 nm), (B), resulting from 7.7×10^{-5} mol/l DPO by combined treatment of γ-rays and continuous gassing of 0.2 mg O_3/ml.min.

Conclusion

The degradation of aqueous DPO, taken as a representative of toxic pollutants produced by combustion of fossil fuels, was studied by ozonolysis as well as by γ-ray under permanent gassing with ozone. Ozone proved to be an efficient oxidizing agent for DPO-decomposition and likewise for the resulting products. The combined action of ozone with γ-ray turned out to be even more efficient in this respect. The involved reaction mechanisms in the step-by-step DPO-degradation is rather complicated. However, some probable reactions are presented for illustration and for better understanding of the manifold processes.

Acknowledgements

This work was performed in the frame of the EU-Research Project EBOGEM, Contract No. ICA2-CT-2000-10005. The authors appreciate very much the financial support, which made the present investigation possible.

Aray H., Aray M., and Sakumoto M. (1986), Exhaustive degradation of humic acid in water by simultaneous application of radiation and ozone. Water Res. **20**, 885–889.

Gehringer P., Proksch E., Eschweiler H., and Sinovatz W. (1992), Remediation of groundwater polluted with chlorinated ethylenes by ozone-electron beam irradiation treatment. Appl. Radiat. Isotopes **43**, 1107–1115.

Getoff N. (1986), Radiation-induced decomposition of biological resistant pollutants in water. Appl. Radiat. Isotopes **37**, 1103–1109.

Getoff N. (1992), Radiation processing of liquid and solid industrial wastes. In: Application of Isotopes and Radiation in Conservation of the Environment. IAEA, Vienna, Austria, pp. 153–169.

Getoff N. (1993), Purification of drinking water by irradiation. A review. Proc. Indian Acad. Sci. (Chem. Sci.) **105**, 373–391.

Getoff N. (1996), Radiation induced degradation of water pollutants. State of the art. Radiat. Phys. Chem. **47**, 581–593.

Getoff N. (1997), Peroxyl radicals in the treatment of waste solutions. In: Peroxyl Radicals (Alfass Z. B., ed.). John Wiley & Sons Ltd., Chichester, England, pp. 483–506.

Getoff N. (2001), Comparison of radiation and photo-induced degradation of pollutants in water: synergistic effect of O_2, O_3, and TiO_2. A short review. Res. Chem. Intermed. **27**, 343–358.

Getoff N. and Seitner D. (1966), Radiation induced carbonilation of aqueous methanol. Z. Physik. Chem. **51**, 27–34 (in German).

Getoff N. and Solar S. (1988), Radiation induced decomposition of chlorinated phenols in water. Radiat. Phys. Chem. **31**, 121–130.

Hoigne J. (1998), Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation process. In: Handbook of Environmental Chemistry (Hrubec J., ed.). Springer, Berlin, Germany.

Krapfenbauer K. and Getoff N. (1999), Comparative studies of photo- and radiation-induced degradation of aqueous EDTA. Synergistic effects of oxygen, ozone and TiO_2. Radiat. Phys. Chem. **55**, 385–393.

Masscheln W. J. (ed.) (1982), Ozonation Manual for Water and Wastewater Treatment. John Wiley & Sons Ltd., Chichester, England.

Rice R. G. and Netzer A. (eds.) (1984), Handbook of Ozone Technology and Application. Kluwer, Dordrecht.

Sanchez M., Getoff N., Sümegi L., and Zona R. (2002), Degradation of aqueous 4-chloroaniline by ozonolysis and combined γ-rays-ozone processing. Z. Naturforsch. **57c**, 1047–1050.

Winarno E. K. and Getoff N. (2002), Comparative studies on the degradation of aqueous 2-chloroaniline by O_3 as well as by UV-light and γ-rays in the presence of ozone. Radiat. Phys. Chem. **65**, 387–395.