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# KINETICS AND MECHANISMS OF POLYETHYLENEGLYCOL FRAGMENTATION BY OZONE IN AQUEOUS SOLUTION

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Abstract—The oxidative fragmentation of Polyethyleneglycol by ozone is investigated by means of batch and semibatch ozonation experiments in the pH range 4.0–9.0. Chemical mechanisms and reaction kinetics of the ozonation processes are determined by also exploiting chemical information from experiments on Diethyleneglycol and Ethyleneglycol ozonation. A kinetic model is proposed capable of describing the fragmentation process due to the direct polymer oxidation by ozone. Copyright © 1996 Elsevier Science Ltd

Key words-polyethyleneglycol, ozone, fragmentation, kinetics, mechanisms

#### INTRODUCTION

Biological methods, which are usually adopted for waste waters treatment, cannot be satisfactorily employed for the abatement of high molecular weight polyethyleneglycol (PEG). The effectiveness of biological degradation processes is strongly or even completely reduced for polymer chains exceeding 10 monomeric units (Suzuki, 1976). Purification of the widely diffused PEG containing waste waters must therefore be demanded to integrated chemical and biological treatments. Preliminary chemical treatments should ensure the reduction of PEG molecular weight by means of reactants capable of causing fast and possibly selective polymer degradation. Ozone is indicated as a valid means for the achievement of this objective (Suzuki et al., 1979). Reported studies however do not cover the whole range of possible ozonation mechanisms, whereas only empirical rate equations are proposed (Morooka et al., 1981) with scarce reference to true mechanistically based reaction kinetics. As a consequence literature studies may hardly serve as an assessment of mathematical models useful for the development of PEG ozonation processes.

In this study the experimental investigations on PEG fragmentation by ozone point to the elucidation of the reaction mechanisms sustaining PEG ozonation and to the assessment of related kinetics. Chemical characterization of PEG ozonation is attempted by submitting suitable model compounds as diethyleneglycol (DEG) and ethyleneglycol (EG)

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to ozonation under experimental conditions which favour either direct or radical oxidation mechanisms.

#### EXPERIMENTAL

800 ml of  $5.0 \times 10^{-4}$  M PEG (10,000 MW) aqueous solutions are submitted to ozonation in a 1 l semibatch stirred reactor as previously described (Andreozzi *et al.*, 1992). 40 Nl/h of an ozonized oxygen stream containing ozone at 4% by vol is continuously fed to the reactor through a gas sparger.

Polymer degradation caused by ozonation is followed by means of Gel Permeation HPLC analysis which allows the number average molecular weight at varying ozonation time to be determined. To this purpose aTSK gel G3000PWXL column flowing with water at 0.4 ml/min is used.

The number average molecular weight of the ozonated PEG samples is evaluated according to a computerized procedure (Cooper, 1989) exploiting molecular weight calibration performed by means of PEG standards ranging from 10,000 to 600 number-average mol.w.

PEG solutions are submitted to ozonation at different pH values ranging from 4.0 to 9.0. Phosphate buffers at constant ionic strength of the resulting solutions are used for pH adjustment. During the ozonation experiments the ozone consumptions at varying ozonation times are evaluated by means of continuous u.v. measurements of the ozone concentration at the outlet of the reactor.

Indications concerning the reaction pathways through which the polymer degradation develops are obtained by analyzing products and intermediates deriving from DEG and EG ozonation. Chemical analyses at different ozonation times are performed by means of HPLC on an Alltech OA-1000 column flowing at 0.8 ml/min with a  $0.02 \text{ N} \text{ H}_2\text{SO}_4$  aqueous solution.

Ozonation kinetics at 293 K of PEG, EG and some EG oligomers are investigated at pH = 4.0 with radical scavenger addition (t-BuOH) in homogeneous batch reacting systems by means of continuous u.v. monitoring of the ozone signal at 260 nm. High concentration ratios of the

organic substrates with respect to ozone are used to obtain conditions of pseudo first order kinetics. For each investigated substrate, different initial concentrations are adopted thus allowing the substrate reaction order to also be determined.

### **RESULTS AND DISCUSSION**

# Chemical investigation

The chemical reactions concerning PEG ozonation are studied by exploiting the simplest PEG-like structure of DEG. Low pH experiments (Fig. 1) performed to investigate the direct ozonation mechanism show that relatively small amounts of C2 fragmentation derivatives (EG, Glycolic Aldehyde, Glycolic Acid) appears as intermediates of the DEG oxidation process. A relevant chromatographic peak belonging to unidentified substances is also observed during DEG ozonation. This peak is likely to comprise DEG uncleaved intermediates of different oxidation degrees as remarked by its persistency in a large range of DEG conversion degrees. A significant increase of EG and Glycolic Acid at equimolar amounts is recorded when the reacting mixture is submitted to severe hydrolytic treatment. This gives evidence of remarkable formation of the EG-Glycolic ester (HOCH2CH2OCOCH2OH) during DEG ozonation.

The presence of only small amounts of C2 derivatives during DEG degradation suggests that these intermediates are much more reactive than DEG. To check this point, ozonation experiments have been performed on EG solutions at the same pH as that of DEG experiments. Results reported in Fig. 2 reveal that both EG and its oxidation derivatives exhibit a reactivity much higher than DEG thus keeping their concentrations at relatively small values in the ozonation experiments of Fig. 1.

The experimental results indicate that the direct DEG ozonation develops according to the following reaction mechanism which also complies with the



Fig. 1. DEG ozonation at pH = 4.0 ○ = DEG,
 △ = Glycolic acid, ☆ = Glycolic aldehyde, □ = EG (after hydrolysis), ◇ = Glycolic acid (after hydrolysis).



Fig. 2. EG ozonation at pH = 4.0.  $\bigcirc$  = EG,  $\square$  = Glycolic aldehyde,  $\triangle$  = glycolic acid.

general indications given by Bailey for the alcohols and ethers ozonation (Bailey, 1982):



Results of DEG ozonation experiments at higher pH values promoting radical oxidation mechanisms are reported in Fig. 3.

A remarkable increase of DEG reactivity is observed at this pH as underlined by the much smaller ozonation time required for complete DEG oxidation. HPLC analyses, although not suitable for quantitative EG evaluation, reveal the presence of relatively higher concentrations of the other  $C_2$ ozonation intermediates with respect to those observed for the oxidation runs of Fig. 1. Higher EG concentrations can be similarly argued despite chromatographic overlapping by other species preventing pure EG signal resolution. HPLC analyses following hydrolytic treatment of the ozonated mixture reveal the presence of intermediate hydrolysable to glycolic acid. Their quantitative evaluation is simply effected by measuring the increase of glycolic acid concentration after the hydrolytic treatment. The more marked occurrence of  $C_2$  derivatives for oxidations runs at pH = 8.0 is a likely consequence of the smaller selectivity of the radical ozonation mechanism with respect to the direct ozonation.

The following reaction mechanism is proposed to explain DEG ozonation leading to primary radical chain formation of EG and hydrolysable DEG oxidation derivatives. Competitive addition of oxygen to radicals A and B has not been taken into account owing to the higher concentration and reactivity of ozone with respect to oxygen.

Last reaction steps leading to olefinic intermediates have been proposed as thoroughly explaining PEG radical ozonation (Morooka *et al.*, 1981). The unique occurrence of this mechanism however is not consistent with the results of our DEG investigation showing side production of intermediates hydrolysable to glycolic acid and EG.

$$O_{3} \xrightarrow{OH^{-}} OH^{-}$$

$$HOCHCH_{2}OCH_{2}CH_{2}OH = CHOCH_{2}CH_{2}OH + O_{2}$$

$$HOCHCH_{3}OCH_{2}CH_{2}OH$$



Fig. 3. DEG ozonation at pH = 8.0.  $\bigcirc = DEG$ ,  $\sum_{i=1}^{k} = Glycolic aldehyde$ ,  $\Box = Glycolic acid$ ,  $\triangle = Glycolic acid (after hydrolysis), <math>\diamondsuit = Intermediates$  hydrolysable to glycolic acid.

Reaction mechanisms similar to those derived for DEG ozonation should refer to PEG ozonation. Diagrams of Fig. 4 show the remarkable polymer degradation at pH = 4.0 and the strong acceleration of molecular weight decay due to the pH enhancement thus indicating the high polymer sensitivity to both direct and radical ozonation mechanism.

#### Kinetic investigation

The results describing the kinetic development of DEG oxidation in batch ozonation experiments are reported in Fig. 5.

Diagrams indicate that reaction kinetics are regulated by first order dependence with respect to ozone. Similar results are obtained for the other investigated substrates, i.e. a linear logarithmic decay of the ozone concentration is observed in each case. Since an equimolar ozone to substrate consumption ratio is involved in the initial step of the direct ozonation mechanism, the general rate equation:



 $-\mathrm{d}C_{\mathrm{L}}/\mathrm{d}t = -\mathrm{d}C_{\mathrm{S}}/\mathrm{d}t = k_{\mathrm{S}}C_{\mathrm{S}}^{\mathrm{n}}C_{\mathrm{L}}$ 

Fig. 4. PEG degradation at varying pH.  $\swarrow$  (pH = 4.0),  $\bigcirc$  (pH = 6.0),  $\square$  (pH = 7.0),  $\triangle$  (pH = 8.8).



Fig. 5. Pseudo first order rate experiments at pH = 4.0 and different DEG concentrations.  $\bigcirc$  (DEG = 0.010 M),  $\square$  (DEG = 0.005M),  $\triangle$  (DEG = 0.002 M),  $\diamondsuit$  (DEG = 0.001 M).

in which  $C_{\rm L}$  and  $C_{\rm s}$  are, respectively the concentrations of ozone and substrate in the liquid bulk, is assumed for the ozonation of each investigated substrate.

The logarithmic plots of the pseudo first order kinetic constants (k') against substrate concentration agree with linearity (Fig. 6) thus allowing the kinetic constants  $(k_s)$  and the substrate reaction orders (n) to be evaluated according to the equation:

$$\ln k' = \ln k_{\rm S} + n \ln C_{\rm S}$$

Reaction orders reported in Table 1 closely approach unity for all but EG substrates. In the same Table are also reported the second order kinetic constants derived for each substrate by assuming a pure first order kinetic dependence and their normalized values with respect to the number of carbon atoms of the substrate molecules ( $k_{CH}$ ).

Kinetic modelling of the PEG degradation process at low pH corresponding to direct ozone attack is performed by assuming that PEG fragmentation is regulated by the rate of the ozone attack to the methylene groups:



Fig. 6. Ozonation kinetics dependence upon substrate concentration at pH = 4.0.  $\triangle = EG$ ,  $\Box = TEG$ ,  $\bigcirc = DEG$ .



The ozone attack is comprehensive of two parallel reactions one leading to immediate polymer cleavage  $(k_1)$  the other to undegraded polymeric structures  $(k_2)$ which can be cleaved by hydrolysis. Polymer fragmentation thus results into two experimental degradation curves, one corresponding to direct cleavage, the other including further cleavage due to hydrolysis (Fig. 7). Mathematical modeling of degradation curves of Fig. 7 is therefore effected by considering that the overall kinetic constant of ozone attack to methylene is split into the individual kinetic components of the two parallel reactions. By assuming that methylene groups reactivity is not appreciably affected by the polymer chain cleavage occurring during polymer degradation, the following rate equation can be singled out to describe PEG degradation in terms of its number average molecular weight decay:

$$d/dt(1/M_n) = 2k(1/M - 1/M_n)C_L$$

where:

 $M_n$  = number average molecular weight M = repetitive unit weight

 $C_1$  = ozone concentration in the liquid bulk k(overall kinetic constant) =  $k_1 + k_2$ .

The above equation is simply derived on the basis of the following considerations. Polymer cleavage is



Fig. 7. Modeling of PEG ozonation at pH = 4.0.  $\bigcirc = M_n$  before hydrolysis,  $\triangle = M_n$  after hydrolysis,  $\diamondsuit =$  Hydrogen peroxide.

caused by the ozone attack to the non-terminal methylene groups. Polymer degradation (also including subsequent hydrolysis cleavage) can be therefore related to methylenes disappearance in the polymer chain. Methylenes concentration can be expressed as a function of the polymer chains concentration (n) and the average polymerization degree  $(X_n)$ :

$$n = m/M_n$$
 (n = moles of polymer/l;  
 $m = \text{grams of polymer/l}$ )  
 $X_n = M_n/M$ 

according to the equation:

$$[CH_2] = 2X_n n - 2n = 2n(X_n - 1)$$
  
= 2m(1/M - 1/M<sub>n</sub>).

The kinetic equation for polymer degradation is therefore given by:

$$-d[CH_2]/dt = -d/dt[2m(1/M - 1/M_n)]$$
  
= 2k[CH\_2]C<sub>L</sub>  
= 2k[2m(1/M - 1/M\_r)]C.

from which:

$$d/dt(1/M_n) = 2k(1/M - 1/M_n)C_L$$

During the entire oxidation process experimental measurements indicate that the ozone concentration in the liquid bulk strictly corresponds with the saturation value. Polymer degradation process thus behaves according to fast ozone mass transfer from the gas to the liquid phase with respect to ozonation kinetics.

By using a best fitting procedure a value of 0.059 and 0.042  $M^{-1}$  s<sup>-1</sup> are estimated for k and  $k_2$ , respectively with a strict correspondence of experimental and calculated results as shown in Fig. 7. As evidenced in Table 1 the overall kinetic constant k closely approaches the values observed for TE-TRAEG and PEG 2000. This indicates that the methylene group reactivity is not affected by the chain lengths of polymers formed by more than three monomeric units.

Substrate	n	ks, 1 mol <sup>-1</sup> s <sup>-1</sup>	k <sub>сн2</sub> , 1 mol <sup>-1</sup> s <sup>-1</sup>
EG	1.28		_
DEG	0.93	0.348	0.087
TEG	0.97	0.468	0.078
TETRAEG	1.01	0.416	0.052
PEG 2000	1.00	5.182	0.057

# CONCLUSION

The possible reaction mechanisms regulating the PEG fragmentation by ozone have been elucidated by submitting PEG and model compounds (DEG, EG) to ozonation at varying pH. The reaction kinetics of the direct ozonation of each investigated substrate have also been established. A remarkably higher reactivity is observed for EG with respect to the other investigated substrates which exhibit similar methylene group sensitivity to the ozone attack. The direct PEG ozonation occurring at lower pH values agrees with reaction mechanisms previously reported for ethers and alcohols. The radical PEG ozonation mechanism promoted by ozone decomposition is observed at higher pH values. The rate equations describing the parallel reaction pathways leading to PEG fragmentation in direct semibatch ozonation are provided.

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#### REFERENCES

- Andreozzi R., Caprio V., D'Amore M. G., and Insola A. (1992) Quinoline ozonation in aqueous solution. Wat. Res. 26, 639-643.
- Bailey P. S. (1982) Ozonation in Organic Chemistry, Vol II, Academic Press, New York.
- Cooper A. R. (1989) Determination of Molecular Weight. John Wiley & Sons, N.Y.
- Morooka S., Ikemizu K., Kishikawa H., and Kato Y. (1981) Degradation rate of poly(oxyethylene) in water by ozone. J. Chem. Eng. of Japan 14, 44–48.
- Suzuki J. (1976) Study on ozone treatment of water-soluble polymers. 1. Ozone degradation of polyethyleneglycol in water. J. Appl. Polym. Sci. 20, 93-103.
- Suzuki J., Taumi N., Suzuki S. (1979) Ozone treatment of water-soluble polymers. 4. Ozone degradability of water-soluble polymers. J. Appl. Polym. Sci. 23, 3281-3288.