

A study on three-phase ozonation

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Abstract. The paper deals with ozone solubility and reactions in octane and octane–water mixtures. It is shown that ozone solubility in pure octane is about twice as high as in water at the same temperature. In two-phase mixtures, 50% of octane and 50% of water, the solubility coefficients of ozone in both phases are close to each other. It was established that during the ozonation of pure octane and octane–water mixtures organic peroxides were formed, which diffused totally from the organic to the water phase. The ozonation of salicylic, benzoic, and stearic acids was studied in octane–water mixtures.

Key words: ozone, solubility, octane, octane–water mixtures, organic peroxides, salicylic acid, benzoic acid, stearic acid, oxidation.

INTRODUCTION

Ozone is applied in three-phase systems where a selective ozone reaction, oxidation of residual compounds and/or enhancement of biodegradability, is required. It can be used to treat drinking water and wastewater, as well as gaseous and solid wastes [1].

In drinking water treatment (particle removal, disinfection) full-scale applications are quite common, while in wastewater treatment sludge ozonation and use of heterogeneous catalyst in advanced oxidation have been applied occasionally.

Current research topics for three-phase ozonation include mainly soil treatment and oxidative regeneration of adsorbents. Ozonation in water–solvent systems has been seldom studied and then only on the laboratory scale [2]. However, this mode of ozonation may be very fruitful in special cases.

The three-phase systems (gas/water/solvent) may be classified by the state of the third phase in water into systems with non-dispersed (segregated) phases

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(fluorocarbons in membrane reactors) and those with the solvent dispersed in water (oil droplets in water–oil emulsions).

The most frequent goals of ozonation in gas/water/solvent systems are [1]:

- to make use of the increased solubility of both ozone and target compounds in the solvent, and thus

- to establish a selective direct reaction between ozone and target compounds.

Two processes occur: (1) a chemical extraction of the organic solute by the solvent followed by ozonation in this phase and (2) the diffusion of ozone from the solvent into water with subsequent reactions.

The feasibility of a water/solvent-phase ozonation depends mainly on the properties of the solvent. The following properties of the solvent should be met:

- low vapour pressure,
- non-toxic and immiscible with water,
- high ozone solubility,
- inertness against ozone.

The achievable selectivity of ozone reactions in gas/water/solvent systems depends much on the distribution of the solute between the gas, water, and solvent phases, which should be checked by partition coefficients from the literature or be determined experimentally. Some information on selectivity is already available from early studies [3]. Inert solvents (e.g. pentane, carbon tetrachloride) provide an opportunity to produce and study typical oxidation products of ozonolysis, such as ozonide [4].

The aim of the present study was to follow the process of ozonation of three typical model compounds depending on their solubility in the solvent (octane) and in water. The compounds selected were salicylic acid (soluble in water, insoluble in octane), benzoic acid (dissolves in water as well as in octane), and stearic acid (insoluble in water, soluble in octane).

EXPERIMENTAL

Experiments on three-phase ozonation were carried out in a bubble column with a volume of 200 mL using the well-known set-up [5]. The flow rate of the ozone–air mixture was kept at 1 L/min with the ozone inlet concentration changing in the range 0.5–12 mg/L. The system under study was octane–water. Octane was chosen as an organic phase because it has low volatility and it is widely used as a solvent.

During experiments the following parameters were determined: concentration of ozone in gas at the inlet and outlet of the reactor, concentration of dissolved ozone in both phases, concentration of hydrogen peroxide in both phases, and concentration of the individual compounds whose ozonolysis was under study.

The concentration of ozone in the gaseous phase was measured at the wavelength 258 nm with a spectrophotometer (UV/VIS Zeiss, Jena, GDR). The concentration of dissolved ozone was determined using the potassium indigo–trisulphonate method [6]. For the determination of the concentration of ozone

Table 1. Methods and conditions of analysis of individual compounds

Compound	Phase	Method	Wavelength, nm
Salicylic acid	Water	Photocolorimetry	525
	Octane	–	
Benzoic acid	Water	Chromatography	276
	Octane	Spectrophotometry	276
Stearic acid	Water	–	
	Octane	Spectrophotometry	230

dissolved in octane 2–5 mL of the sample was intensively shaken with the water solution of indigo during 1 min. Ozone extracted from octane and dissolved in water solution was measured photocolometrically.

The concentration of hydrogen peroxide was measured according to [7] using TiSO_4 solution. The concentration of peroxide in octane was also determined after the extraction of 2–5 mL of the sample with water solution of titanium sulphate.

The initial concentration of organic acids was 1 mM. Their decay during ozonation was followed according to the methods and conditions given in Table 1.

Chromatographic analysis of benzoic acid was carried out on HPLC Millichrom (Nauchpribor, USSR) equipped with a UV-spectrophotometer (190–360 nm). A chromatographic column with a length of 64 mm and diameter of 2 mm was filled up with 5 μm Separon C18 (Chemapol, Czechoslovakia). The eluent (100 $\mu\text{L}/\text{min}$) contained 50% of acetonitrile and 0.1% of acidic acid in water. For the determination of salicylic acid concentration the photocolometric method with trivalent iron was used according to [8].

RESULTS AND DISCUSSION

Solubility of ozone

For the description of ozonation processes in a three-phase system gas/water/solvent it is necessary to know the solubility coefficient of ozone in each of the liquid phases as well as its partition coefficient between the phases.

It is now generally accepted among ozone researchers that the average solubility coefficient of ozone α_w ($\alpha_w = C_L^*/C_G$) in water at 20°C is 0.24 [9]. At the same time only very limited data are available for ozone solubility in organic solvents including octane. For this reason a series of tests of ozonation of water-free octane was carried out at the temperature of 20°C varying the ozone concentration in the inlet gas from 0.5 to 4 mg/L. It was established that the ozone solubility coefficient in octane α_{OCT} was 0.51 ± 0.04 , i.e. approximately twice as high as that in water at the same temperature.

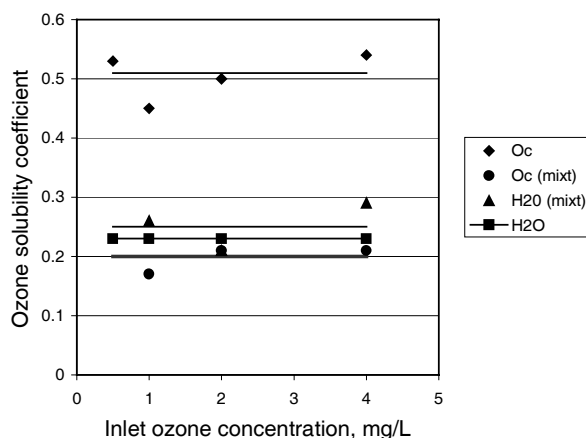


Fig. 1. Ozone solubility coefficient α versus the ozone inlet concentration in the gaseous phase. Oc – in dry octane; Oc (mixt) and H2O (mixt) – in octane–water mixtures (50% + 50%), and H2O – in water.

However, when dealing with a three-phase system (gaseous ozone is the third one), it is also necessary to know the solubility of ozone in two-phase mixtures, such as 50% of octane and 50% of water. The corresponding experiments showed that the solubility coefficients of both phases were close to each other, and for the whole range of the inlet ozone concentration in gas the coefficients were 0.25 ± 0.11 for water (α_w) and 0.20 ± 0.10 for octane (α_{oct}) (Fig. 1).

Formation of peroxides during ozonation

During the experiments we observed an interesting phenomenon – differently from ozonation in distilled water, the measured value of the liquid phase ozone concentration depended here significantly on the time spent on the analysis procedure, i.e. the measured concentration increased with time.

Obviously some organic peroxides which reacted with indigo solution were formed during the ozonolysis of octane. It was noted by Bailey [3] already in 1958 that many organic compounds produce hydroperoxides on ozonation. This is predicted also by the Criegee mechanism [4]. As peroxides were formed we determined their concentration in the organic (octane) as well as in the water phase during the process. It was established that the peroxide formed during the ozonation of octane–water mixtures was totally transformed from the organic to the water phase. Therefore, later the peroxide concentration was measured only in the water phase.

The results of these experiments are shown in Fig. 2. This figure illustrates the increase in peroxide concentration when ozonizing pure (dry) octane and the mixture of 50% octane and 50% water. It was ascertained that the concentration of peroxide formed depends only on the dose of the consumed ozone, and not on the ozone concentration in the inlet gas.

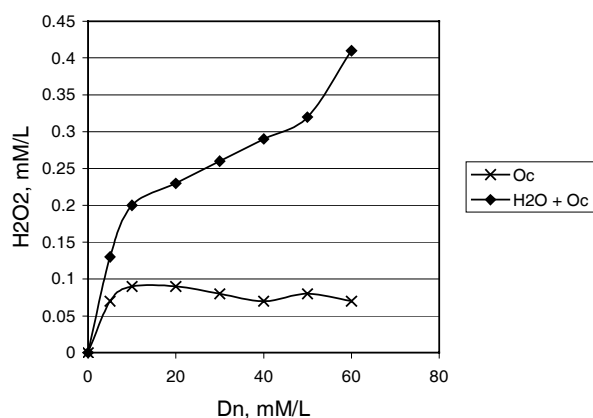


Fig. 2. Formation of organic peroxides in the ozonation of dry octane (Oc) and octane–water mixture (H₂O + Oc, 50% + 50%) versus the ozone dose consumed D_n.

Oxidation of model compounds

As during the ozonation of octane–water mixtures (organic) peroxides were formed, it was assumed that these could be a very efficient additional oxidant for some target organic compounds. The following model compounds were chosen:

- salicylic acid (does not dissolve in octane),
- benzoic acid (dissolves in octane as well as in water),
- stearic acid (dissolves in octane, does not dissolve in water).

The ozonation of these organic acids yielded quite interesting results. First, the experiments with a preozonized octane–water mixture indicated that during 24 h neither the concentration of peroxides nor that of salicylic acid changed. This means that the peroxides did not react directly with salicylic acid if there was no dissolved ozone in the mixture.

Figure 3 shows that addition of some octane to the 1 mM solution of salicylic acid increases somewhat the pseudo-first order reaction rate of salicylic acid with ozone (the constant increases from 5.3×10^{-3} to $6.4 \times 10^{-3} \text{ s}^{-1}$), probably due to the impact of the peroxide formed. However, there is no further increase in the reaction rate constant value starting with the octane content of 20% in the salicylic acid–water solution.

Benzoic acid was chosen as a model compound soluble in both phases, in water as well as in octane. Figure 4 shows that benzoic acid dissolved in dry octane does not react with ozone at all, whilst in water its reaction with ozone proceeds at a high rate.

However, when carrying out ozonation of benzoic acid in water solution in the presence of octane (50% of octane, 50% of water) quite a different picture can be observed. The concentration of benzoic acid in water solution is reduced at a much higher rate than in the case without octane. At the same time an increase in the benzoic acid concentration in octane is taking place due to its redistribution between phases (Fig. 5).

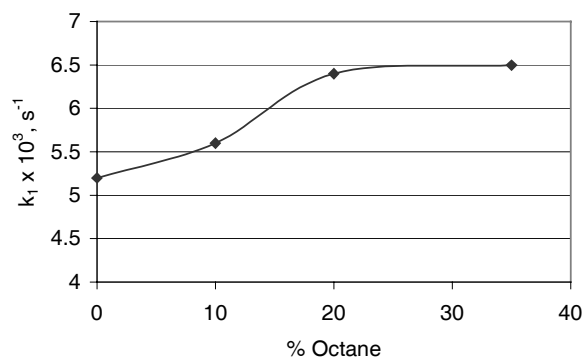


Fig. 3. Pseudo-first order reaction rate constant of salicylic acid ozonolysis versus the octane concentration in the octane–water mixture.

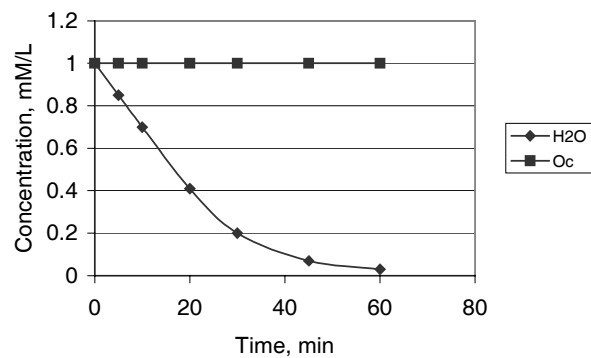


Fig. 4. Ozonation of benzoic acid in octane (Oc) and in water (H2O) (inlet ozone concentration 4 mg/L).

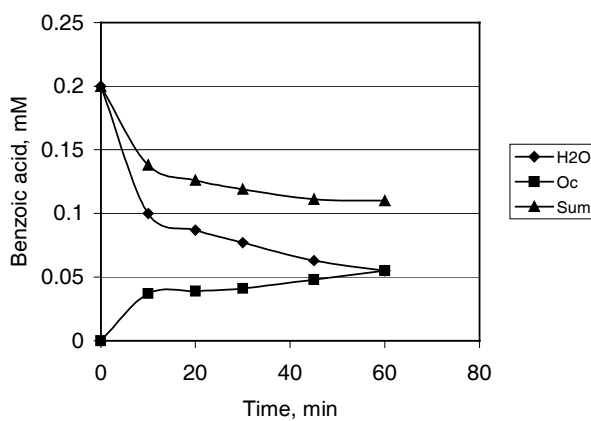


Fig. 5. Ozonation of benzoic acid in octane–water mixture (50% + 50%).

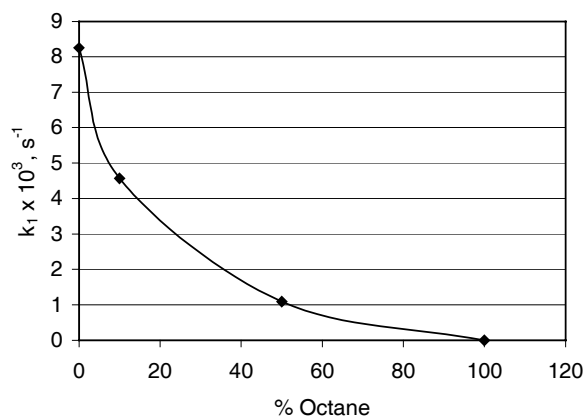


Fig. 6. Pseudo-first order reaction rate constant of benzoic acid oxidation versus the octane concentration in the octane–water mixture.

The rate of the reduction of the total benzoic acid concentration in the reaction mixture (50% of octane, 50% of water) is significantly lower than the rate in water (Fig. 6). Thus, even a small admixture of organics is unfavourable for the ozonation of benzoic acid.

Stearic acid represented model compounds that do not dissolve in water but dissolve very well in octane. According to our experiments stearic acid in dry octane did not react with ozone; however, addition of some water to the octane phase brought about a chemical reaction with ozone. The maximum value of the reaction rate constant of stearic acid ozonation ($k_1 = 1.6 \times 10^{-3} \text{ s}^{-1}$) was obtained at the water content of 10% in the octane–water mixture. Further increase in the water content in the reaction mixture did not have any considerable impact.

Thus, different organic acids behave differently in this three-phase system. Their behaviour depends on their solubility in the organic and the water phase.

CONCLUSIONS

The solubility of ozone in octane at the temperature of 20°C is about twice as high ($\alpha_{\text{OCT}} = 0.51$) as that in water at the same temperature. In two-phase mixtures, such as 50% of octane and 50% of water, the ozone solubility coefficients in both phases were close to each other, and for the whole range of the inlet ozone concentration in gas were equal to 0.25 ± 0.11 for water (α_{W}) and to 0.20 ± 0.10 for octane (α_{OCT}).

It was established that the organic peroxides formed during the ozonation of octane–water mixtures totally diffused from the organic to the water phase. The concentration of the peroxides formed depended only on the dose of the consumed ozone, and not on the ozone concentration in the inlet gas. At the same time the amount of peroxides formed was several times higher in the case of ozonation of dry octane than in the case of ozonation of octane–water mixtures.

In octane–water systems the target compounds selected depending on their solubility in octane and in water (salicylic acid, benzoic acid, and stearic acid) behaved all towards the organic peroxide as additional oxidants with the ozonation in different ways.

ACKNOWLEDGEMENT

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Osoonimine kolme faasilises süsteemis

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On käsitletud osooni lahustumist ja reaktsioone oktaanis ning süsteemis oktaan–vesi. On näidatud, et osooni lahustuvus puhtas oktaanis on peaaegu kaks korda suurem kui vees samal temperatuuril. Kahefaasiliste segude puhul (50% oktaani ja 50% vett) olid osooni lahustuvuskoeffitsiendi väärtused mõlemas faasis teineteisele lähedased. Katsetel selgus, et puhta oktaani ning oktaani ja vee segude osoonimisel tekkisid orgaanilised peroksüüdid, mis kohe ja täielikult difundeerusid oktaanist vette. Peroksüüdide kontsentratsioon olenes ainult neeldunud osooni doosist, mitte aga osooni kontsentratsioonist sisenevas gaasis. Tekkinud peroksüüdide kogus oli puhta oktaani osoonimisel mitmeid kordi suurem kui oktaani ja vee segude osoonimisel. Valitud mudelainete (salitsüülhape, bensoehape ja steariinhape) käitumine osoonimisel kolme faasilises süsteemis oli erinev, kuid viitas kõigil juhtudel orgaanilise peroksüüdi kui täiendava oksüdeerija tekkele.