

## CHAPTER II

### THEORETRICAL CONSIDERATIONS

#### Production processes [2-4]

##### 1. Production of benzaldehyde

Benzaldehyde is produced principally by the hydrolysis of benzal chloride or the partial oxidation of toluene. There are other manufacturing processes, but at present they have no industrial importance.

##### 1.1 The hydrolysis of benzal chloride



##### 1.2 The partial oxidation of toluene



The choice among different processes depends on the size of the plant and end use of product. For a chlorine-free product, vapor phase oxidation is the best process. It has lower production and plant costs compared to the liquid phase oxidation route. For small-scale production, liquid phase oxidation by the batch process is suitable. On a small-scale, the hydrolysis of benzaldehyde is the cheapest if chlorine-free benzaldehyde is not required. In the large-scale production of phenol by the Dow process and of  $\epsilon$ -caprolactam by the Snia Viscosa process via the toluene-benzoic acid synthesis route, considerable

amounts of benzaldehyde are formed as a by product. Benzaldehyde is readily oxidized to benzoic acid in air and should be stored under nitrogen. Tanks of benzaldehyde should be made of aluminum or stainless steel. Benzaldehyde can be transported in drums with baked enamel finishes or in tanks made of aluminum or stainless steel.

Benzaldehyde is commercially available in two grades (Table 2.1). *Pure* benzaldehyde which is suitable for most uses, accounts for more than 95% of amount sold. *Double-distillated* benzaldehyde is used mainly in the pharmaceutical, perfume, and flavor industries and must therefore be partially pure and free from foreign odors.

**Table 2.1** Purity specification of benzaldehyde grades.

Property	Industrial grade	
	Pure	Double -distillation
Assay, wt%	> 99.0	> 99.5
Benzoic acid, wt%	< 0.3	< 0.1
Water, wt%	< 0.3	< 0.1
Chlorine, wt%	< 0.02	< 0.007
Color (APHA)	< 20	< 20

## 2. Production of benzoic acid

Practically all of the benzoic acid in the world is now produced by the catalytic, liquid phase oxidation of toluene with molecular oxygen. The oxidation produces several by products. Benzaldehyde is formed in fair amounts, especially at lower conversions. It can be recovered by distillation. A limited amount of benzyl alcohol is formed, but its recovery is not practical because of unavailable esterification with benzoic acid. Benzyl benzoate can be

recovered from the bottom residue of the benzoic acid column. The usual commercial forms of benzoic acid are flakes or the molten liquid. The flakes are generally packed in 25 kg paper bags or in flexible containers. The molten benzoic can be transported in stainless steel vessels.

There are two categories of quality specifications for benzoic acid, i.e., for technical use in bulk quantities and for pharmaceutical use. The current actual quality of commercial benzoic acids from several sources, together with the Japanese specifications JIS K 4127, are shown in Table 2.2. More precise quality specifications are necessary for pharmaceutical and food additive uses. In Table 2.3, JP 10 specifications are shown. It should be noted that minor differences exist in other countries. For example, the arsenic content is sometime specified.

**Table 2.2** Quality specification for benzoic acid intended for technical use.

Items	JIS K 4127	Specifications for commercial products			
		Japan	USA		Europe
		commercial grade	Industrial grade	Technical grade	commercial grade
m.p., °C	120-123	121-123	121-123	121-123	122-122.5
Assay, %min.	98	99.6	97.5	99.0	99.5
Ash, %min.	0.1	0.01	0.01	0.01	0.01
Chlorobenzoic acid, %max.	1.0	none	none	none	none
Phthalic acid, %max	0.5				
Appearance	white	off-white	brownish yellow	white	white

**Table 2.3** Quality specifications for benzoic acid intended for pharmaceutical use.

Assay (by alkali titration)	99.5% min.
Appearance	white crystals
Odor	none or insignificant
Iron (III) chloride test	pass test
Solubility in ethanol, acetone, ether, or chloroform	pass test
m.p., °C	120-124
Heavy metals (as sulfides)	pass test
Chlorinated compounds (by ignition with CaCO <sub>3</sub> )	pass test
Readily oxidizable substances (by permanganate)	pass test
Phthalic acid (by fluorescence with resorcinol)	pass test
Color stability (by sulfuric acid)	pass test
Weight loss on desiccation	0.5% max.
Ignition loss	0.05% max.

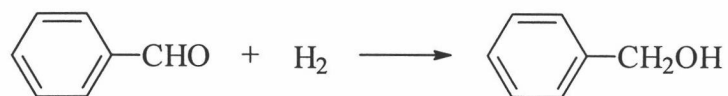
### 3. Production of benzyl alcohol

Benzyl alcohol can be produced in many ways. At present there are only two processes of substantial industrial importance.

#### 3.1 The hydrolysis of benzyl chloride



## 3.2 The hydrogenation of benzaldehyde



The industrial production of benzyl alcohol by the hydrogenation of benzaldehyde gained importance because substantial quantities of benzaldehyde were available as a by product of the production of phenol (Dow process) and  $\epsilon$ -caprolactam (Snia Viscosa Process) by the oxidation of toluene. Benzyl alcohol is stored in stainless steel tanks. Because benzyl alcohol is oxidized readily, it is advised to cover the surface of the liquid with nitrogen. Benzyl alcohol can be transported in drums protected by stoving finishes and in tank wagons of stainless steel.

Several grades of benzyl alcohol are commercially available (Table 2.4). *Technical* grade is obtained from the first and last fractions in the distillation of the crude alcohol, it has little importance. *Pure* benzyl alcohol is most important grade in terms of volume and is required for most applications. *Double-distilled* benzyl alcohol is used mainly in the perfume and pharmaceutical industries and must therefore be exceptionally pure and free of foreign odors. In recent years the *photographic* grade has become increasingly important.

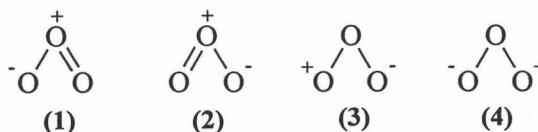
**Table 2.4** Specification for certain grades of benzyl alcohol.

Compound	Grades			
	Technical	Pure	Double-distilled	Photographic
Benzyl alcohol	> 97.0	> 99.0	> 99.8	> 99.5
Benzaldehyde	< 0.5	< 0.2	< 0.04	< 0.03
Chlorine	< 0.2	< 0.02	< 0.01	< 0.005
Dibenzyl ether	< 2.0	< 0.05	< 0.02	< 0.02

## Ozonization reaction [5-8]

### 1. Occurrence and Properties of Ozone

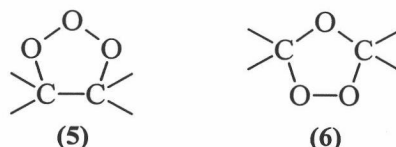
Ozone occurs in the atmosphere, but its concentration is too low for the atmosphere to be the practical source. Ozone is a colorless gas and a dark blue liquid. It has a characteristic sharp odor which is detected by the nose at a level that provides warning of toxic exposure. It dissolves in many solvents and resulting concentrated solutions become blue at low temperatures. The ozone molecule is nonlinear with a bond angle of  $116^\circ$ . In contrast to oxygen, it is not paramagnetic and resonance forms that contribute to its structure possess pair electrons. From (1) and (2) with a coordinate bond to the third oxygen might be expected to make a greater contribution, but (3) and (4) possess a terminal oxygen with only six electrons which account for the electrophilic nature of ozone exhibited in many of its reactions.



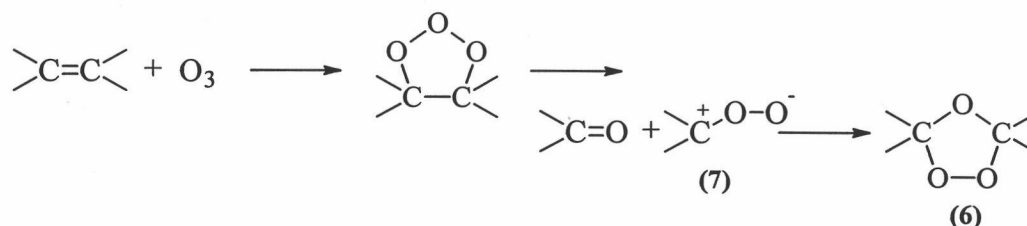
### 2. Reaction of Ozone

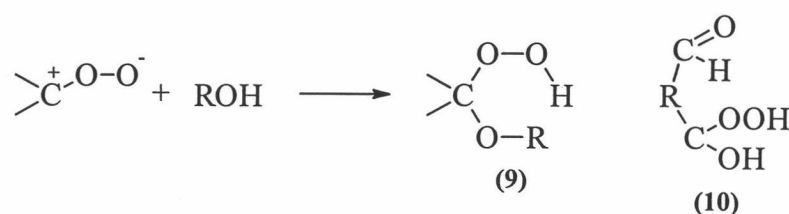
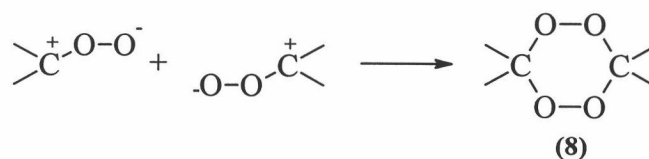
The value of ozone as an oxidant for olefins was established by Harries during the first decade of this century. As a result of his work, ozonization has become a standard method for the location of double bonds in carbon molecules. Ozone attacks many inorganic as well as organic structures and is now widely used as an oxidant on a laboratory scale. Industrial application has been limited, but are increasing. Ozonization or ozonation is a general term that

refers to the reaction of ozone with a substrate. Ozonolysis is ozonization in which there is a cleavage of a bond. Molozonide, primary ozonide, and initial ozonide are synonymous terms which refer to the 1,2,3-trioxolane structure (5). Ozonide refers to the 1,2,4-trioxolane structure (6).

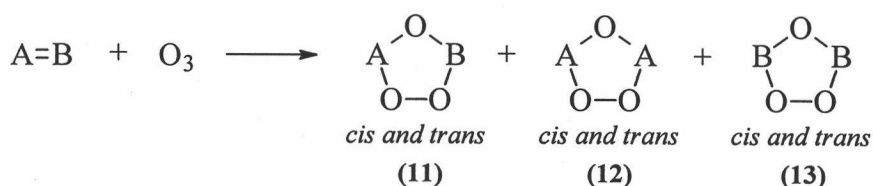


The reaction of ozone with olefins usually results in cleavage of the double bond and formation of aldehydes, ketones, and/or carboxylic acids depending on the reaction conditions and the structure involved. A reaction path was suggested by Criegee et al., which not only explained ozonide formation but all other products of ozonization reactions known at the time as well. Criegee suggested that ozone attacks a double bond to form an initial product which cleaves to an ionic ozonolysis intermediate (7) and a carbonyl compound (aldehyde or ketone). The stabilization of the ionic ozonolysis intermediate is determined by the solvent used. In the case of aprotic solvents the stabilization proceeds by reaction with the carbonyl group to cyclicozonide (6) or by intermolecular polyaddition to polyozonides or mixed polyperoxy ozonides or by cyclodimerization (8), while protic solvents undergo direct addition with the ionic intermediate. This gives, in addition to aldehydes or ketones, hydroperoxy derivatives (9) and in the case of cyclic olefins-terminal  $\omega$ -carbonyl hydroperoxy derivatives (10).





For the ozonization of an unsymmetrical olefin, the cleavage may occur in two ways and recombination could lead to six ozonides. Structure (11) is a normal ozonide, (12) and (13) are cross ozonides.



Ever since Harries demonstrated the practical applications of the ozonization reaction, it has been used as the basis for certain analytical procedures. It has proved particularly valuable for the quantitative analysis of carbon-carbon unsaturation and for the determination of double bond positions. The analysis for unsaturation has broad applications and it is of special importance in lipid chemistry.

In practice ozonization usually requires three experiment steps : (1) the generation of ozone, (2) the introduction of ozone into the reaction mixture, and (3) the isolation of products.



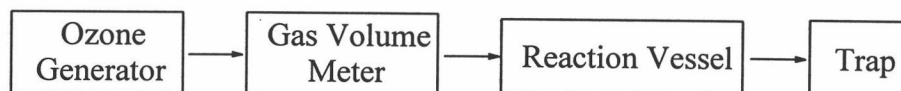
## 2.1. Ozone generation

Ozone is produced at a spark gap, but it cannot be conveniently isolated. Ultraviolet and shorter wavelength radiation also causes oxygen to undergo conversion to ozone, which may be used for environmental sterilization. High concentration of ozone are obtained by the electrolysis of sulphuric and perchloric acids. Most of ozone prepared industrially, in laboratory and for water purification, is produced by silent electric discharge.

Generators based upon the silent discharge principle usually resemble the device built originally by Siemens in 1857. In this apparatus ozone was produced by allowing oxygen to pass between two electrodes separated by insulation, which is usually glass. A high voltage alternating current produces an alternating ion flow resulting in the conversion of oxygen into ozone, which is swept out by the oxygen stream. The concentration of ozone produced in this manner is directly proportional to the voltage and pressure of oxygen, provided sufficient cooling this available for heat dissipation. The purity of the oxygen feed determines the concentration of ozone produced by silent electric discharge. Air gives only half as much ozone as pure oxygen for the same electrical energy input. This suggests that pure oxygen is preferred. In large-scale use, however, the waste would be great, since well over 90% of the oxygen input would be lost, unless the unused oxygen was recycled.

## 2.2. Introduction of ozone

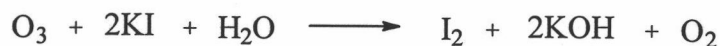
Ozone may be introduced into the reaction in a variety of ways, but it is usually introduced by bubbling the gaseous reagent through a solution of the compound to be ozonized. A conventional system consists of the source of ozone, the reaction vessel, a trap, and a gas volume meter.



The reaction vessel is designed so that a gas may enter through a submerged outlet in the solution and after passing through the solution escape at the surface. A gas-washing bottle is appropriate and provides an exit at the top so that the effluent gas may then pass to the trap. Cooling is usually required and the gas-washing bottle may be placed in a bath or a vessel may be used with either an external cooling jacket and/or an internal cooling well.

Solvents ranging from pentane to water have been used in ozonization. Those which have been found to be generally useful are acetic acid, ethyl acetate, the chlorinated methanes, and the lower alkanes. Because the ozone is such a strong oxidant, it is difficult to find a solvent which will not react with it to some extent.

The trap is usually another gas-washing bottle following the reaction vessel. Its purpose is to decompose excess ozone that may escape from the reaction. Any one of a number of substances may serve this purpose, but a potassium iodide solution is usually used. Ozone that escapes from the reaction passed through the KI solution and causes a brown color to develop because of oxidation of  $I^-$  to  $I_2$ .



In spite of the heterogeneous nature of the ozonization reaction, ozone uptake by most olefins is very fast. In this cases color development in the trap indicates the end of the reaction. A known amount of the ozone may be added to the reaction if the concentration from the generator is known. This may be determined by a photometric or iodometric method ; the latter is usually used,

and the iodine that is freed by ozone from potassium iodide is determined by thiosulphate titration.



Since iodine is produced by ozone on a mole-for-mole basis, 2 moles of thiosulphate are required for 1 mole of ozone. If concentration is calculated in terms of millimoles of thiosulphate per liter of gas sample, the similar concentration of ozone is obtained by dividing by 2.

$$\text{ozone concentration millimoles/liter} = \frac{[\text{S}_2\text{O}_3^{2-}] \times \text{ml S}_2\text{O}_3^{2-}}{2 \times \text{gas sample volume in liters}}$$

Concentration in milligrams per liter is obtained by multiplying by the molecular weight of ozone.

$$\text{ozone concentration mg/liter} = \frac{[\text{S}_2\text{O}_3^{2-}] \times \text{ml S}_2\text{O}_3^{2-} \times 48}{2 \times \text{gas sample volume in liters}}$$

The percent of ozone in the gas sample may be calculated from concentration in millimoles per liter.

$$\% \text{ ozone} = \text{millimoles O}_3/\text{liter} \times 0.0224 \times 100$$

### 2.3. Isolation of products

The isolation of products from the ozonization reaction can be accomplished in many ways. In many cases the product or products of ozonization are either the ozonide itself or some peroxide resulting from reaction with a participating solvent. Decomposition methods are used if the ozonide is to be avoided and only substances derived from it are desired. In some case the ozonide is so unstable that it spontaneously decomposes in the

reaction mixture ; in other cases there is a question whether the ozonide ever forms since only carbonyl-cleavage products are isolated.

The general decomposition methods are : (1) reductive, (2) hydrolytic, (3) oxidative, and (4) thermal. The choice of method is determined by the nature of the olefin and the products desired. For example, if the olefin has a hydrogen on at least one of the olefinic carbons, then an aldehyde or a carboxylic acid may be obtained, depending upon the type of decomposition. If the aldehyde is desired, then the reductive decomposition would be used. To obtain the carboxylic acid an oxidative work-up should be selected. Hydrolysis is the best method to avoid oxidation or reduction of the initial decomposition product, provided the ozonide will decompose under this condition.

Reductive decompositions have been reported using almost every reducing agent known; to name a few : various metal-acid combination, sulfite ion, bisulfite ion, lithium aluminium hydride, sodium borohydride, zinc dust and glacial acetic acid, Raney nickel, iodide ion, stannous chloride, Grignard reagents, triphenylphosphine, trimethylphosphite, and boranes, as well as catalytic hydrogenation under a variety of conditions and with a number of catalysts. The selection of a reductive method of decomposition is determined by many factors, the most important one being the nature of the product desired and its sensitivity in turn to the reducing agent.

### **Literature reviews**

Catalytic hydrogenations of ozonides are usually carried out at atmospheric pressure with palladium or platinum catalyst. Henne and Perilstein [9] found that ozonides were reduced with palladium supported on calcium carbonate to give high yield of aldehydes, ketones and acids. Methylene chloride could not be used because it prevents catalytic hydrogenation. Cook

and Whitmore [10] have found that Raney nickel alone will effectively reduce ozonides to aldehydes or ketones when a solution of ozonide in pentane was added to a suspension of Raney nickel in pentane.

Sulfite ion has been used as a reducing agent toward ozonization products. Effective use was made in the case of ozonization of vinyl pyridine to give the corresponding aldehyde in good yield [11]. The alkyl-substituted vinyl pyridines give higher yields of pyridinecarboxaldehydes than the unsubstituted vinyl pyridines.

A general procedure for the reductive decomposition of the ozonization products using lower trialkyl phosphites has been found by Thomson [12]. The reaction was conducted at  $-40^{\circ}\text{C}$  after ozonization of the olefin in methanol followed by reduction with trimethyl phosphite.

Papas et al. [13] reported that hydroperoxides from ozonolysis of olefins in aprotic solvent such as methanol were reduced to aldehyde with dimethyl sulfide. The reaction was carried out under neutral condition at low temperature. Any excess dimethyl sulfide was readily removed by evaporation (b.p.  $32^{\circ}\text{C}$ ) and the by products, methanol and dimethyl sulfoxide, cause no purification problem.

Hydrolytic decomposition of peroxide ozonization products is the basis of the method that Subluskey et al. [14] have developed for synthesizing aromatic aldehydes from olefins in high yield. The intermediate ozonization product is decomposed by steam, thus eliminating the necessity of reduction step. The nature of intermediate is not established, but since methanol is present it is suggested that a peroxyacetal is possible and it is hydrolyzed by steam. Sturrock et al. [15] have prepared diphenaldehyde by ozonization of a slurry of phenanthrene in methanol. The work-up involved the addition of water followed by solvent removal to give a 93% yield of the aldehyde. It is noteworthy that no reducing agent was required.

Zinc has been used more often than other reducing agent for the reductive decomposition of ozonides. Harries used this reagent in his pioneering studies, and worker ever since has found it to be extremely useful when one wishes to avoid oxidative conditions. Henne and Hill [16] recommended that the ozonide be added dropwise to suspension of zinc dust in acetic acid. Under these conditions, ketones or aldehydes were generally obtained in yield of sixty to seventy percent.

Wilms found that the peracetic acid was an effective oxidative reagent for decomposing ozonization products. Both peracetic acid and performic acid have been used, with performic acid being preferred. Bailey [17] has prepared adipic acid by ozonolysis of cyclohexene and followed by oxidative decomposition in formic acid medium. By using hydrogen peroxide, an 85% yield of nearly pure adipic acid was obtained.

Dicarboxylic acids may be prepared by the ozonization of cyclic olefins. If the reaction was conducted in an emulsion of sodium hydroxide and hydrogen peroxide, the ozonide intermediate was destroyed as it was formed. Such technique has been devised by Fremery and Fields [18]. In the emulsion ozonization method cycloolefins was converted to dicarboxylic acid in good yield. As the ring size of the cycloolefins increases, the yield of expected carboxylic acid increases. Open chain olefins react equally well under these condition. 1-Octene gave heptanoic acid in 75% yield.

In Habib et al.'s opinion [19] the method of Odinkov et al. for synthesis of dicarboxylic acid by ozonolysis of cycloalkenes with 1 molar equivalent of ozone in an ether-type solvent; followed by hydrogenation over Lindlar's catalyst has no advantage over standard methods. They obtained 75-80% yields of dicarboxylic acids by the simpler and cheaper method of ozonizing cyclohexene with 1 molar equivalent of ozone in a 9:1 mixture of glacial acetic acid and formic acid at 10°C, followed by the passage of molecular oxygen through the reaction mixture at the reflux temperature.

Lithium aluminium hydride and related reducing agents may be used for decomposition if the corresponding alcohol instead of carbonyl products are desired. Sousa and Bluhm [20] reported that the ozonide of oleic acid which treated with both sodium borohydride and lithium aluminium hydride was obtained different decomposition products. With more reactive lithium aluminium hydride, the acid group was reduced.

White et al. [21] examined the ozonolysis of olefins in reactive solvents methanol or 1-butanol, followed one vessel, two-stage catalytic hydrogenation over platinum catalyst or Raney nickel. Under carefully controlled conditions this sequence of reactions provides a general method for the synthesis of alcohols in excellent yield.

Gupta et al. [22] reported a procedure for the reaction of hydroperoxide products of olefin ozonolysis giving aldehydes in yield comparable to those obtained by dimethyl sulphide. Since ozonolysis of olefins in methanol generates essentially  $\alpha$ -methoxyhydroperoxides or related peroxydic products thiourea appeared to be a suitable reagent for their reduction to carbonyl end products.

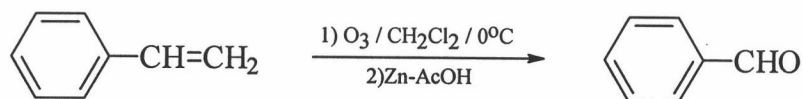
### Ozonolysis of styrene [23-26]

Reaction of ozone with styrene had been studied previously. Keaveney et al. reacted styrene with ozone at  $-65$  to  $-75^{\circ}\text{C}$  in the presence of methanol and determined the reaction products, which consisted of benzaldehyde, formaldehyde, and two peroxides. All four compounds were produced in equal amounts, and it was concluded that ozone could cleave the double bond to give the aldehyde and zwitterion with equal likelihood. Painter et al. observed that the ozonolysis of styrene gave three ozonides (of styrene, stilbene and ethylene) in relative amounts 93:1:6.

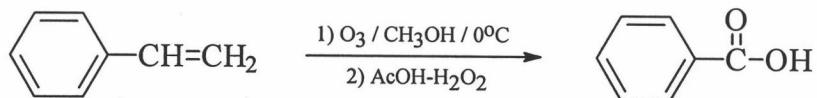
More studies on the kinetics of ozonization of styrene in  $\text{CCl}_4$ , confirm the 1:1 stoichiometry of the olefin-ozone reaction. This indicates that the phenyl ring is not appreciably attacked by the ozone under the experimental condition.

### Synthetic Reaction

#### 1. Preparation of benzaldehyde from styrene



#### 2. Preparation of benzoic acid from styrene



#### 3. Preparation of benzyl alcohol from styrene

