

## CHAPTER 2

### APPLICATIONS OF OZONE IN WATER AND WASTEWATER TREATMENT

Rip G. Rice

In this chapter the various applications for ozone in treating drinking water and industrial and municipal wastewaters will be described. It is important to understand specific aspects of the properties of ozone, and how and where ozone is applied in the various treatment process steps, because these factors all affect the selection of appropriate analytical methodologies for determining concentrations of ozone or other parameters by which the ozonation processes can be controlled.

For example, in disinfecting drinking water, ozone normally is applied near the end of the treatment process when the ozone demand of the water is very low. Under such conditions, a residual concentration of dissolved ozone is developed in less than a minute. This residual can be measured accurately, reproducibly, and is used routinely in European and Canadian drinking water treatment plants to monitor and automate the ozone disinfection process step.

On the other hand, when ozone is used to oxidize impurities, such as iron and manganese, it is applied at an early stage in the water treatment process, sometimes before the total ozone demand has been satisfied. Although a measureable residual of ozone eventually can develop during this oxidative treatment, its measurement, monitoring and control are complicated by the high levels of insoluble and colored materials which result from oxidation and hydrolysis of the cations to be removed. As a consequence, the process must be monitored and controlled by an analytical procedure other than measurement of dissolved ozone residual.

Similarly, when ozone is used to disinfect secondary effluents (which have very high ozone demands), disinfection sometimes can occur before the ozone demand has been satisfied. In addition, foaming and precipitation of suspended solids can interfere with measurement of dissolved ozone residual concentrations, even if they develop. As was the case with the oxidation of iron and manganese, this type of disinfection process also must be monitored by some measurement other than dissolved ozone residual.

These aspects of ozone analytical technology will be discussed in the following chapter, to introduce more detailed presentations of the methodologies of ozonation in subsequent chapters of this monograph.

#### FUNDAMENTAL CHARACTERISTICS OF OZONE RELEVANT TO WATER AND WASTEWATER TREATMENT

Ozone ( $O_3$ ) is an unstable gas at the temperatures and pressures encountered in water and wastewater treatment plants. It has a characteristic, pungent odor, which is not offensive. In the Earth's stratosphere, ozone is formed photochemically, but it occurs at ground levels only in low concentrations, primarily by photochemical decomposition of certain transient air pollutants.

At ambient temperatures, ozone is a blue-colored gas, but at the low concentrations at which it is generated commercially at its point of use, this color is not noticeable unless the gas is viewed through a considerable path length.

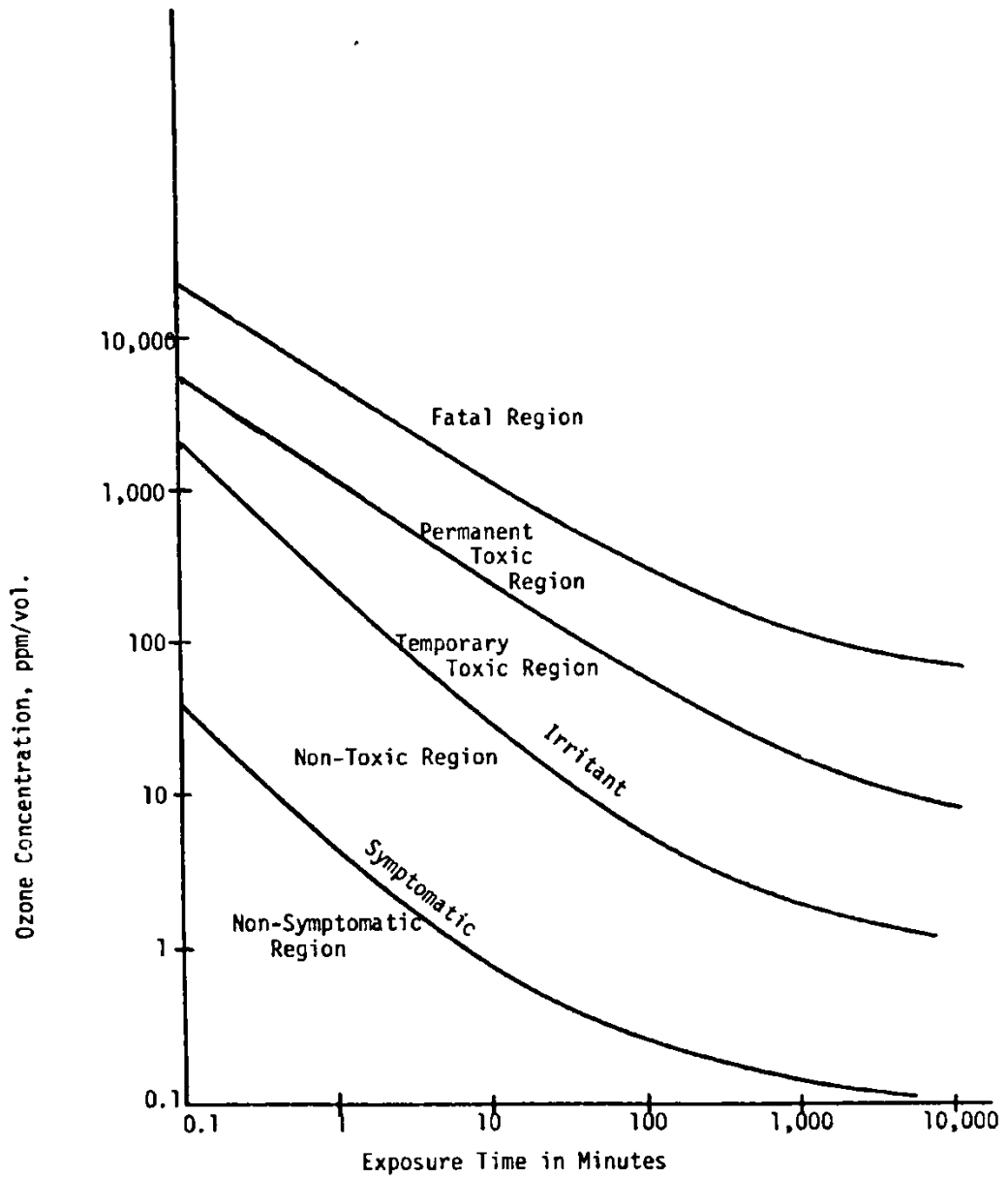
Pure ozone melts at a temperature of  $-192.5^\circ\text{C} \pm 0.4^\circ$  and boils at  $-111.9^\circ\text{C} \pm 0.3^\circ$  (Manley and Niegowski, 1967). At  $-112^\circ\text{C}$ , pure ozone condenses to a dark blue liquid that explodes easily. Less concentrated ozone-oxygen mixtures (above 20% ozone) also are explosive, either in the vapor or liquid state. Such explosions may be initiated by small amounts of catalysts, organic matter, shocks, electrical sparks, or sudden changes in temperature or pressure.

However, under the conditions whereby ozone is generated in water and wastewater treatment plants, concentrations of ozone above 9 to 10% cannot be obtained conveniently. No instances of ozone explosions have been reported during the past 100 years of its use in treating drinking water in various countries throughout the world.

#### TOXICITY OF OZONE TO HUMAN BEINGS

The major concern for exposure to ozone is breathing it when ozone has leaked accidentally into the atmosphere where people are working. This can happen if ozone contacting systems are improperly designed, if improperly chosen materials are used to construct equipment to handle air or oxygen containing ozone, or if leaks develop in pipe joints and fittings carrying ozone-containing gases. If ozone is detected in the workplace atmosphere, the appropriate response procedure is to shut off the electrical power to the ozone generators. This immediately ceases the production of ozone. Strategically placed fans now can exhaust the workplace atmosphere of ozone. Startup of the fans can be arranged to be triggered by a signal from the ambient air ozone monitor.

Figure 1 (Langerwerf, 1963) shows the various concentration/time relationships for human exposure and responses to ozone. Exposure to atmospheric ozone levels below 1 ppm for as long as 10 minutes is



non-symptomatic. Exposure to levels of 100 ppm for 10,000 minutes, or to 10,000 ppm for 30 seconds, can be fatal. Normally, human olfactory capabilities can detect ozone in the ambient air at levels of about 0.1 ppm.

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Bollyky (1978) has discussed the biological effects of human exposure to ozone at levels and exposure times in the symptomatic zones of Figure 1. These effects include increased pulmonary flow resistance, decreased carbon monoxide diffusing capacity, and decreased lung elasticity. Exposure to 1.5 to 2 ppm of ozone for two hours produces dryness of mouth and throat, constrictive type chest pains, lessening of mental ability, difficulty in coordinating and articulating, loss of appetite, coughing, and 13% loss of vital capacity. However, recovery from these symptoms usually is complete within one to 14 days.

Breathing ozone produces enzymatic changes in blood, fragilizes red blood cell membranes and causes increased oxidation of unsaturated fatty acids. Cytologically, no chromosomal aberrations have been noted, nor is there evidence for carcinogenic, mutagenic, or teratogenic effects or effects upon reproduction. Occupational exposure to ozone causes irritation of eyes, nose and throat, coughing, headaches, lethargy, with soreness and pulmonary edema, after severe exposures. In addition, slight decreases in night vision and slight increases in peripheral vision have been noted after exposure to ozone.

### STABILITY OF OZONE

In the gaseous state, ozone has a relatively long half-life (about 12 hours in the ambient atmosphere), but in aqueous solution its half-life is much shorter. There are statements in the ozone literature to the effect that ozone has a 20-minute half-life in distilled water. There is little doubt that the purer the water, the lower the concentration of ozone-demanding constituents that will be present, and the longer will be the apparent half-life of ozone.

Figure 2 (Rosenthal, 1974) compares the half-life of ozone in double-distilled water, once-distilled water, tap water, raw groundwater, and two filtered lake waters, all measured at 20°C.

It can be seen that the half-life of ozone in water can vary from about 10 minutes in filtered lake waters, to considerably greater than one hour in double-distilled water.

Because of the inherent instability of ozone, it cannot be purchased and stored until ready for use as can other oxidants/disinfectants currently employed. Instead it is generated on-site, near its point of use, as it is required.

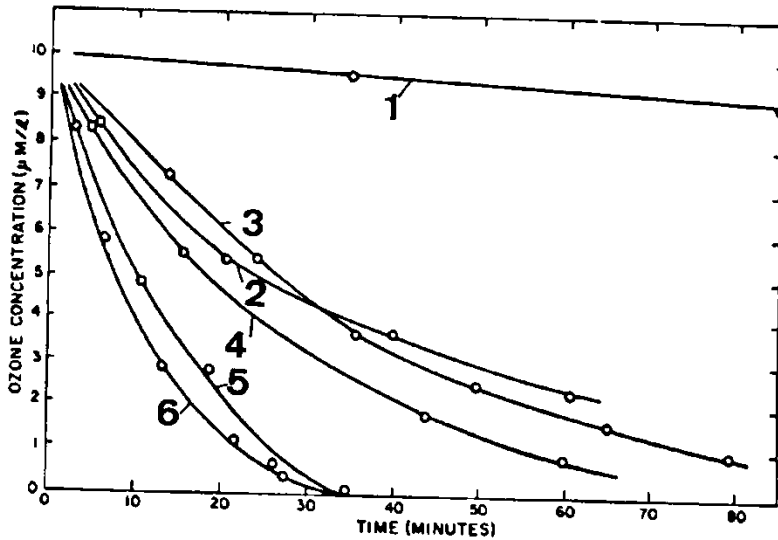


Figure 2. Decomposition rates of ozone in various types of water at 20°C: 1 = double-distilled water; 2 = distilled water; 3 = tap water; 4 = low hardness groundwater; 5 = filtered water from Lake Zürich; 6 = filtered water from the Bodensee (Rosenthal, 1974).

**SOLUBILITY OF OZONE IN WATER**

Venosa and Opatken (1979) have discussed Henry's law, the fundamental relationship governing the solubility of ozone (or any gas) in water. Expressed simply, Henry's Law states that, at constant temperature, the weight of any gas that will dissolve in a given volume of liquid is directly proportional to the partial pressure the gas exerts above the liquid (Sawyer and McCarty, 1978).

Expressed as an equation:

$$Y = HX$$

- where
- Y = partial pressure of the gas above the liquid (mm Hg)
  - X = concentration of the gas in the liquid at equilibrium with the gas above the liquid (mol gas/total mol gas + liquid)
  - H = Henry's law constant, which varies with temperature (mm Hg/mol fraction).

The terms in the above equation can be converted into units of concentration, such that:

- Y = concentration of gas above the liquid in equilibrium with the gas dissolved in the liquid (mg/L)
- X = concentration of gas in the liquid in equilibrium with the gas above the liquid (mg/L)
- H = [mg gas/L gas]/[mg gas/L liquid].

Thus Henry's law simply expresses the relationship between the concentration of gas above the liquid that must exist for a given concentration of gas to be dissolved in the liquid. The lower the value of H, the more soluble is the gas.

After converting Henry's law constants (taken from the International Critical Tables) to units of concentration, Venosa and Opatken (1983) compared the solubilities of oxygen and ozone (generated at a concentration of 1% in air) in water at temperatures of 0°, 10°, 20°, and 30°C (see Table I). The magnitude of Henry's constant is a function of temperature alone, not of concentration.

TABLE I. SOLUBILITY OF OZONE AND OXYGEN IN WATER  
ACCORDING TO HENRY'S LAW

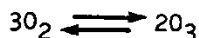
gas	temp. °C	H	Y	X
		mg gas/L air/ mg gas/L water	mg gas/L air	mg gas/L water
oxygen (air)	0	20.4	299	14.6
	10	25.4	289	11.4
	20	29.9	279	9.3
	30	34.2	270	7.9
ozone (1.0 wt.%)	0	1.56	12.9	8.3
	10	1.86	12.5	6.7
	20	2.59	12.1	4.7
	30	3.80	11.7	3.1

The values of H for oxygen in Table I are the same, whether the gaseous-phase oxygen concentration is 21% (air) or 100% (pure oxygen). It is clear from the data of Table I that ozone is approximately 13 times more soluble than oxygen at standard temperatures and pressure (H = 20.4 for oxygen versus 1.56 for ozone) over the temperature range presented.

#### GENERATION OF OZONE

Although there are several methods by which ozone is generated for application to water and wastewater treatment, the corona discharge method is the most widely used procedure. This is because the corona discharge procedure produces the highest concentrations of ozone for the amount of electrical energy applied.

In the corona discharge technique (Figure 3), a dry, oxygen-containing gas (usually air in drinking water treatment plants, but pure oxygen in many large sewage treatment plants) is passed between two electrically charged plates separated by a ceramic dielectric medium and a narrow discharge gap. Under these conditions, part of the oxygen is converted to ozone:



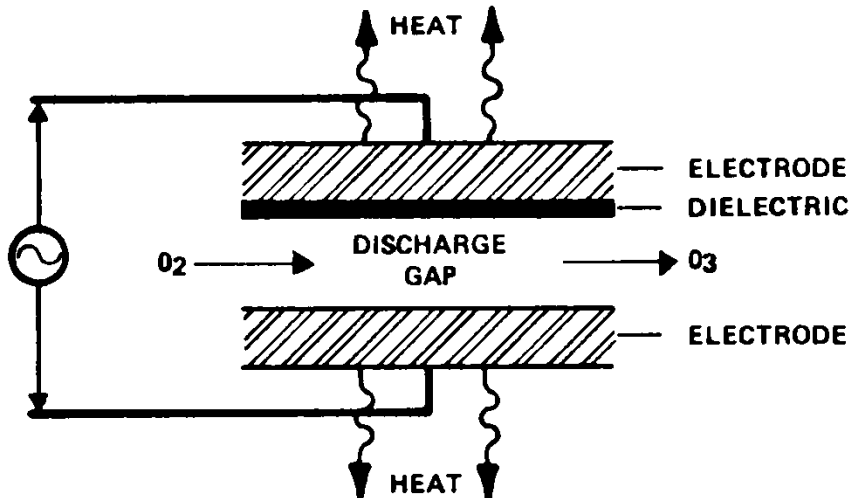


Figure 3. Schematic diagram of ozone generation by the corona discharge procedure.

The synthesis of ozone proceeds by an equilibrium reaction, and the rate of the reverse reaction increases rapidly above 35°C. During generation of ozone, a considerable amount of heat also is liberated; therefore it is critical that the generator be adequately cooled, in order to maximize the yield of ozone. This normally is accomplished with chilled water, but it can be accomplished also with air.

By the corona discharge procedure described above, concentrations of ozone of 1% to 3% are produced when air is the generator feed gas, and 2% to 6% when pure oxygen is the generator feed gas. Therefore, one analytical requirement in ozone technology is for methods which will allow determination of the relatively high concentrations of ozone in air or oxygen as produced by the ozone generators.

For a more detailed discussion on the generation of ozone, the reader is referred to a recent treatise by Carlins and Clark (1982), and to several presentations included in Masschelein (1982a).

**APPLICATIONS OF OZONE IN DRINKING WATER TREATMENT**

Uses of ozone listed in this section have been discussed in detail by Rice *et al.* (1981). Specific applications will be described here to introduce the types of analyses which are required for control of the ozonation steps, and which will be discussed in detail in subsequent chapters.

Table II lists the many applications for ozone which are being practiced in operational drinking water treatment plants. Generally, these applications can be characterized into three types, disinfection, chemical oxidation, and pretreatment of the water for biological treatment. This last application can be considered to be a special case of chemical oxidation.

TABLE II. APPLICATIONS OF OZONE IN DRINKING WATER TREATMENT

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**Disinfection**

Bacterial Disinfection  
Viral Inactivation

**Oxidation**

Removal of Soluble Iron and Manganese  
Decomplexing Organically-Bound Heavy Metals (Mn, Fe, etc.)  
Color Removal  
Taste and Odor Removal  
Algae Control  
Organics Control (Pesticides, Phenols, Detergents,  
THM Precursors, etc.)  
Destruction of Inorganics (Cyanides, Sulfides, Nitrites)  
Microflocculation (Precipitation of Dissolved Organics) Removal  
of Suspended Solids

**Preparation for Biological Processing**

Nitrification  
Reduction in Levels of Dissolved Organics

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**Bacterial Disinfection and Viral Inactivation**

When used for these applications, ozone is applied at the end of the water treatment process. This means that chemical addition, flocculation, sedimentation, and filtration all have been conducted prior to the water being ozonized. Consequently, the water being disinfected normally is very clean and free of high concentrations of oxidizable organic materials, other than the microorganisms to be killed (bacteria) or inactivated (viruses).



When ozone is applied to waters of this cleanliness, a residual concentration of ozone quickly develops in the treated water (less than a minute). This residual is stable in the contacting chamber(s) and shortly thereafter.

French public health authorities have adopted a residual ozone standard for drinking water treatment plants in which ozonation is employed for disinfection/viral inactivation. The ozone demand of the water is satisfied and a residual ozone concentration of 0.4 mg/L is developed during a period of at least four minutes of contacting. This 0.4 mg/L residual then is maintained for an additional minimum period of four minutes. Under these conditions, viruses have been shown to be more than 99.9% inactivated (Coin, *et al.*, 1964, 1967). Within the periods of time involved during ozonation (minimum 8 minutes), bacteria are easily killed, and the drinking water is effectively sterilized.

In operational drinking water treatment plants, ozone disinfection/viral inactivation normally is accomplished using two or more side-by-side contacting chambers. The 0.4 mg/L level is attained in the first chamber, then is maintained in the second or subsequent chambers. In normal practice, the four minute contact time is at least doubled, to eight to 12 minutes, to insure that the required disinfection conditions have been achieved. About two-thirds of the total ozone used for disinfection is fed to the first contact chamber, in which the influent water has the highest ozone demand, and the balance to the second chamber.

#### Ozone Oxidation Reactions

Most of the applications of ozone for chemical oxidation are installed at early stages of drinking water treatment, because of the formation of insoluble oxidation products which are removed during later sedimentation, flocculation, coagulation and/or filtration steps.

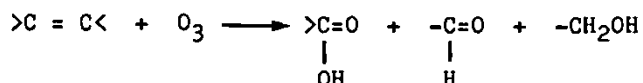
In many cases the materials being oxidized by ozone react rapidly. Such impurities as iron, manganese, many organics which cause objectionable tastes and odors, many phenols, some organic complexes of heavy metals, many types of algae, and inorganic impurities such as cyanide, sulfide, and nitrite, all react with ozone nearly instantaneously. In such cases, the development of a measureable concentration of ozone can be taken as an indication of complete oxidation of the impurity(ies) to be removed. However, there is no standardized requirement to attain a specific level of residual ozone, as with viral inactivation. Measurement of levels of dissolved ozone well below 0.1 mg/L will suffice to indicate that the ozone demand of the water has been satisfied.

On the other hand, some types of organic materials react slowly with ozone. These materials include many detergents, many pesticides, some organo-nitrogen compounds, THM precursors (humic and fulvic acids), and some types of algae. Under these circumstances, measureable levels of residual ozone can develop quickly. However, the presence

of residual ozone in these cases is not indicative of complete reaction, and therefore is meaningless in terms of monitoring the ozonation process.

### Microflocculation

During ozone oxidation of most organic materials, it is only rarely that the oxidation proceeds to completion under drinking water treatment conditions, with total conversion of organic carbon to  $\text{CO}_2$ . Ozone oxidation proceeds with the introduction of oxygen into the organic structures, producing oxygen-containing carboxyl, carbonyl, or hydroxyl groupings:



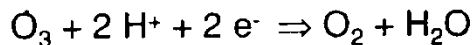
All of these oxygen-containing moieties are quite polar and negatively charged. Because of the negative charges, they are susceptible to combining with themselves by hydrogen bonding, and also with soluble polyvalent cations normally present in water supplies, such as calcium, magnesium, iron, aluminum, manganese, etc. Such combinations of soluble polyvalent cations, and organics containing a plurality of carboxyl, carbonyl and hydroxyl groupings produce insoluble materials. If sufficient hydrogen bonding occurs between oxidized molecules, higher molecular weight adducts can form, which also may precipitate from solution.

Thus in many cases, ozonation of clear waters produces water of increased turbidity.

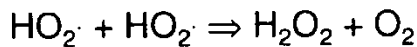
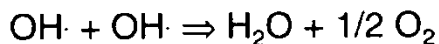
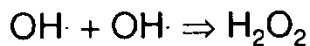
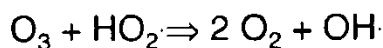
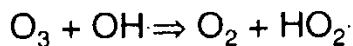
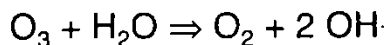
### Removal of Suspended Solids

Small, colloidal particles are maintained in suspension by surface charges which are similar (all positive or all negative). Ozonation can change surface charges from positive to negative. If only small doses of ozone are applied in these situations, partial conversion of positive surface charges to negative charges will occur, thus maximizing the coagulation of oppositely charged suspended compounds. Thus in many cases, ozonation of turbid waters will cause a type of flocculation, resulting in lower turbidity.

Whether ozonation will cause microflocculation or removal of suspended solids will depend upon the specific composition of the waters being treated.



è di + 2,07 volts, uno dei più elevati esistenti. Quindi l'ozono è un ossidante estremamente potente. Alternativamente, viene sottoposta alla scarica l'aria secca. Si ottiene una miscela azoto-ossigeno-ozono che può essere parimenti utilizzato. L'ozono si decompone in acqua in diversi modi:

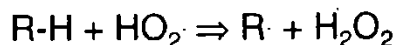
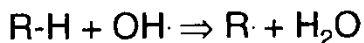


L'insieme di queste reazioni fa sì che l'ozono si decomponga in acqua secondo l'equazione:

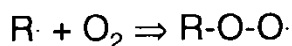
$$-d[\text{O}_3]/dt = k^\circ [\text{OH}\cdot]^{0.55} [\text{O}_3]^2$$

Si calcola che in acqua pura l'ozono abbia, a temperatura ambiente, un tempo di vita media di 25 min ed una solubilità di  $10^{-2}$  moli  $\text{L}^{-1}$

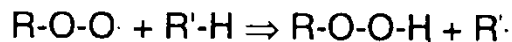
Le specie reattive nell'ossidazione con ozono sono l'ossidrile radicale  $\text{OH}\cdot$  e l'idroperossilradicale  $\text{HO}_2\cdot$ . Queste specie sono dei potenti estrattori di atomi di idrogeno, anche da legami carbonio-idrogeno non attivati, per dare radicali



Questi radicali vengono poi catturati dall'eccesso di ossigeno formando alchilidroperossilradicali:



che estraggono altri atomi di idrogeno secondo le caratteristiche di una reazione radicalica a catena (autoossidazione):



L'idroperossido ROOH si decompone poi formando prodotti di demolizione. Particolarmente efficiente sembra l'azione dell'ozono nei riguardi dei composti aromatici.

## OZONE DISINFECTION OF DRINKING WATER

**Jean-Pierre Légeron**

Fouras, France

The first observations mentioning ozone's disinfecting property for drinking water date back to the end of the last century. In 1886 De Meritens noted a reduction in levels of microorganisms after ozonation [1]. A large amount of research, both fundamental and applied, has since confirmed the findings of these initial experiments. Among the most important works are Katzenelson et al. [2] in Israel, and Sproul and Majumdar [3] in the United States.

Unanimity thus has gradually been established as to ozone's destructive action on microorganisms in water. Ozone may be said to act blindly, since no limits to disinfection have been found in the numbers or species eliminated. Such universality, which obviously is related to the application conditions, may be explained by the mode of action of ozone: in contrast to the usually employed halogens, ozone does not have a reversible inhibitor effect on intracellular enzymes. Because of its very high oxidation-reduction potential, this disinfectant acts as an oxidant of the constituent elements of cell walls before penetrating inside microorganisms and oxidizing certain essential components (e.g., enzymes, proteins, DNA and RNA) [4,5]. When a large part of the membrane barrier is destroyed, the bacterial or protozoan cells lyse, which results in their destruction.

If the membrane barrier is only slightly damaged, it may be repaired by the bacterial cell, which may explain the revival phenomena that sometimes are noted. Finally, by attacking such diverse elements as plasmodia, viruses, trophozoids, cysts, spores or cellular aggregates,

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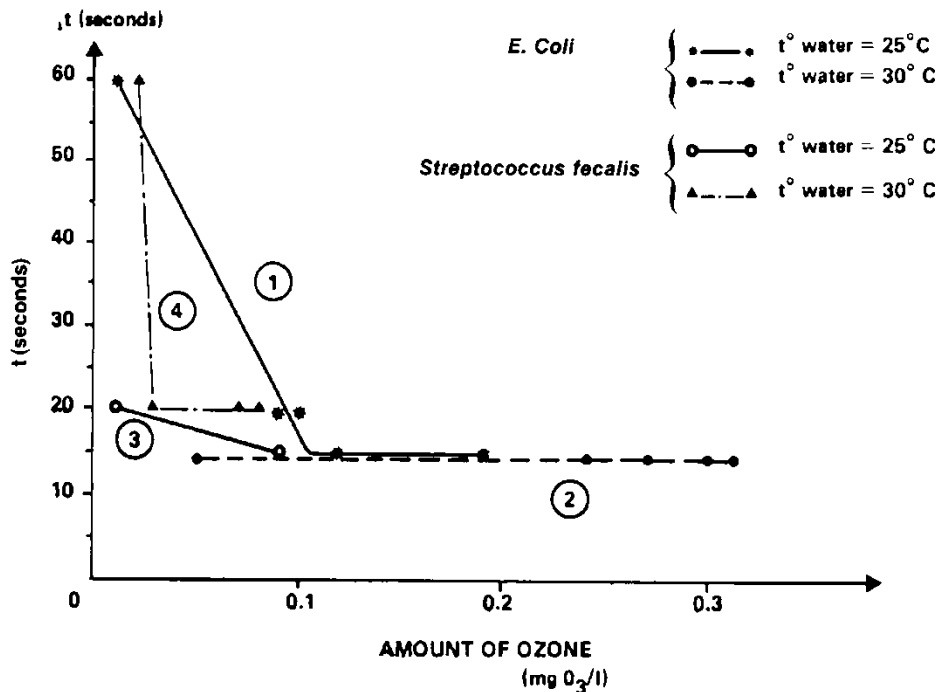
ozone provides a barrier to the transmission of diseases, a barrier that can be maintained with absolute safety only if the previously defined ozonation conditions are properly applied.

### DRINKING WATER DISINFECTION

On the basis of observations made, various studies have allowed definition of the exact parameters that were and are generally applied in drinking water treatment using ozone disinfection.

#### Experimental Origins

Sulzer et al. [6] have shown through their laboratory work that the extent of germ inactivation is related both to the contact time of these microorganisms with ozone and to the aqueous ozone concentration ( $RO_3$ ) (Figure 1 [7,8]). Relationships of the kind " $RO_3 \times CT$ " were reported without it being possible to establish a precise universal law.



**Figure 1.** Bacterial destruction through ozonation (after Kinman [7], according to Drapeau and Paquin [8]).  $t$  = time for total destruction of microorganisms in pure water.

### OZONE DISINFECTION OF DRINKING WATER 3

Thus, for the same contact time, the ozone concentration necessary to obtain a 99.99% inactivation might vary from 1 to 100, depending on the type of organism (virus, bacteria, yeast, etc.). Similarly, for a given species, a ratio of 10 may be attained [8], depending on whether it is vegetative or not. The problem is further complicated when the microorganisms appear in aggregate form or when they cling to suspended matter. Thus, for heavily loaded waters, relationships of the following kind have been established [9]:

$$\ln\left(\frac{N}{N_0}\right) = a \ln(TT) + b(RO_3) + c$$

where  $N, N_0$  = number of germs at time  $t$  and  $t_0$   
TT = the quantity of ozone injected into the water  
a,b,c = constants that depend on the medium containing the microorganisms and the ozonation conditions.

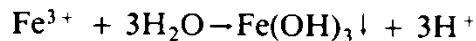
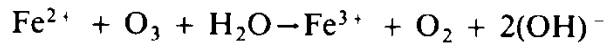
Because drinking water is lightly contaminated as compared with wastewater,  $RO_3 \times CT$  is satisfactory in practically all cases. Thus, when it becomes  $25 \text{ mg-hr/m}^3$ , any water treated with physical and chemical processes and then ozonated may be considered perfectly safe according to French public health criteria.

of day and especially on the time of year. Thus, the ozonation system must be flexible enough to always provide proportionally sufficient ozone to assure a residual of 0.4 mg/l. Flowrates may vary in a ratio of one to two or more, so it is advisable to provide several treatment lines operating in parallel, which may be operated as needed. The ozone transfer into water thus remains optimum. However, ozone contact columns never should be kept full of water when the diffusion is not running, to avoid any formation of deposits on the porous diffusers.

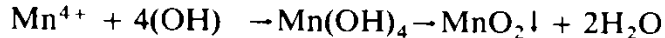
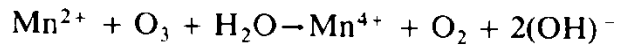
A water's quality is never really constant, and its ozone demand varies constantly. The undesirable effects of suspended solids on disinfection are well known as well [9,15,16]. Most pretreatment processes now in use before ozone disinfection do remove larger particles, but colloidal particles are still found in pretreated water. The switchover to rapid filtration from slow filtration, which was commonly used in the past, is partly responsible. Many microorganisms have a tendency, to different degrees, not only to bunch together among themselves but also to cling to suspended matter in water. These suspended particles thus create a protective effect, and the disinfectant is sometimes powerless against microorganisms with which it has difficulty remaining in contact for the necessary time. This may explain the kinetics of microorganism removal [8,9,17]: the microorganisms are often decomposed in an initial phase, which is very rapid and destroys more than 99.9% of the germs. A second, slower phase follows and results in total destruction. It may easily be imagined that when water contains particles whose size is above 50 microns, it is possible to detect some plate-count germs in it after true ozonation (0.4 mg O<sub>3</sub>/l for 4 min). It is therefore important that, when necessary, water be well pre-treated with the usual means for removing colloidal particles (flocculation, sedimentation and filtration) prior to ozonation for disinfection. A water of excellent physicochemical and bacteriological quality thus will be ensured.

## CHEMISTRY OF IRON AND MANGANESE OXIDATION WITH OZONE

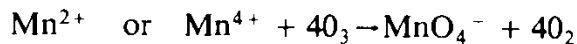
Ferrous iron is oxidized rapidly by ozone to ferric ions, which, at neutral pH, will hydrolyze, coagulate and precipitate as ferric hydroxide according to:



Similarly, divalent manganous ions are oxidized to manganic ions, which then hydrolyze, forming the insoluble manganese dioxide:



However, excessive ozonation of manganese compounds produces very water-soluble septavalent permanganate ion, which is pink in color in dilute solution:



Once permanganate forms, however, it can oxidize dissolved organics that still may be present, slowly reverting back to the manganic form, which, in turn, forms insoluble manganese dioxide. Alternatively, if the permanganate solution is passed through a bed of GAC, the permanganate will be reduced rapidly to form  $\text{MnO}_2$ :





## ESTIMATING TASTES AND ODORS

The terms "odors" and "tastes" often are considered together by water treatment engineers. It would be less confusing to refer to the two problems separately. Rosen et al. [1] have recalled that there are in fact four true taste sensations: salty, sweet, sour and bitter; the factor called taste in drinking water most often corresponds to odors (due to a back-olfaction phenomenon). Confusion exists because odor is sensed when the water flows in the tester's mouth.

Tastes often are produced by substances whose concentration is hard to measure by the usual chemical techniques. For example, several algae, cyanophyceae in general, release phenolated substances that already may be ill-smelling by themselves, but which, in particular, may form chlorinated compounds (chlorophenols) during water disinfection. The flavor of these compounds may make the water unfit for consumption

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even if their concentration in the water is below the threshold value measurable analytically. This phenomenon was especially investigated by Burttschell et al. [2]. In practice, research conducted on this subject tends to determine the nature of the substances which impart odors and tastes to water.

Montiel [3] showed that, in practice, compounds with highly different formulas may induce the same sweet taste (Figure 1). Conversely, compounds with only very small formula variations may produce highly different tastes (Figure 2). Moreover, the intensity of a taste or odor obviously depends on the concentration of the odorous substance, but it is not directly proportional to it. This phenomenon was studied in sensorial psychology and is expressed by the Weber-Fechner law:

$$R = K \log S$$

or by Steven's law:

$$R = K S^n$$

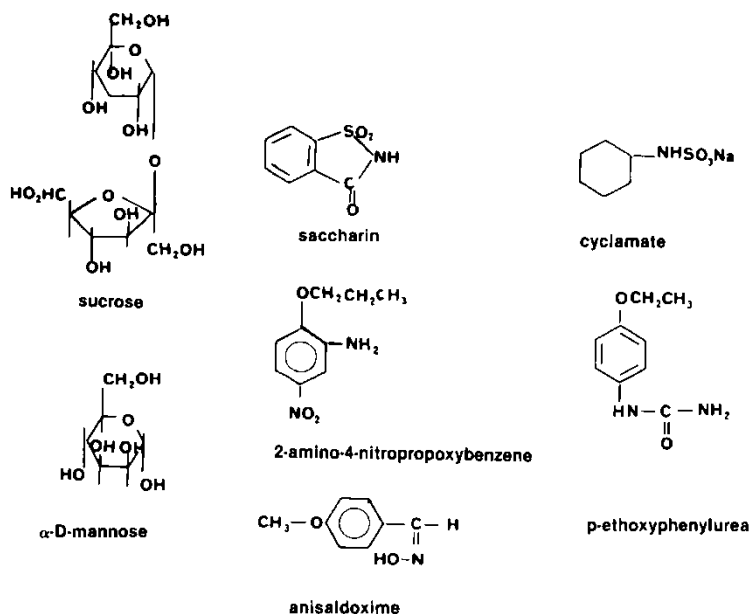
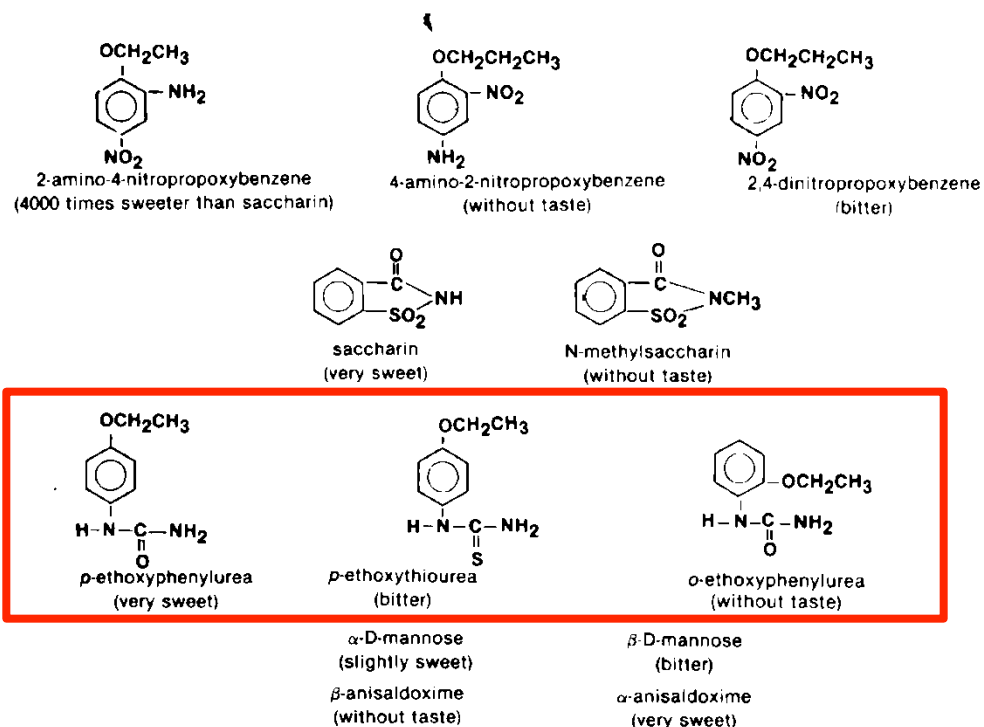


Figure 1. Structure of several sweet-tasting compounds.



**Figure 2.** Small variations in structure and changes in taste.

where  $R$  = intensity of a taste or odor  
 $S$  = concentration of odorous substance  
 $K$  = constant  
 $n$  = coefficient relating the decrease in human response as the concentration of offensive substance increases.

$$R = K \log S$$

As far as olfaction is concerned,  $n$  is far below 1, and depends somewhat on the odorous substance, but more on the individual being tested.

Therefore, the Weber-Fechner or Stevens laws show that olfaction and/or taste thresholds will be more representative factors of pollutant concentration in water than of initial odor or taste intensities before dilution. Moreover, the simultaneous presence of several compounds may modify the ratio between the concentration of the product responsible for the phenomenon, and the intensity of taste and/or odor for the second parameter may be enhanced by interaction phenomena. Rosen et al. [4] and Baker [5] noticed this for various organic compounds, while Von Sydow [6] ascertained this fact for foods.

In practice, the intensity of water taste is ascertained after dilution, and the water is tasted at a temperature that depends on different standards. Moreover, it is necessary that the water be tasted by various tasters selected as a function of their gustatory sensitivity.

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Whether they are of metabolic or industrial origins, the substances are generally organic and their concentrations in the water are very low since the scale of concentrations ranges from nanogram- to microgram-per-liter levels.

### ORIGIN OF TASTES AND ODORS

Mouchet [7] presented a bibliographical study on tastes and odors of biological origin. These may have various sources:

- metabolites secreted by certain microorganisms (actinomycetes, algae);
- decay of vegetation or microorganisms; or
- industrial and agricultural wastes.

The two main causes are industrial effluents and metabolites. Lin [8,9] observed that the taste and odor problems of metabolic origin are more prevalent in stagnant waters, while those resulting from pollution are more typical of running waters. Rosen et al. [1] confirmed this point of view by comparing the water in the Grand Lac (Ohio) and that from its outlet (the Wabash river), and noticing that the tastes and odors due to microorganisms developed, especially in the lake.

### Determination of Odorous Substances

Sigworth [10] has shown the importance of the problem raised by bad tastes in a survey of 241 installations in the United States. A summary of his results is shown in Table I.

Table I. Causes of Tastes and Odors in U.S. Water Supplies [10]

Cause	Number of Installations	Percentage
Algae	198	82
Decay of Vegetation	162	67
Industrial Waste	92	38
Other Causes	55	23

### *Actinomycetes*

Actinomycetes are the major elements responsible for bad tastes and odors. They are present in all surface waters in which *Streptomyces* and *Micromonospora Nocardia* predominate. The species most frequently mentioned for taste and odor problems is *Streptomyces*. Berthelot and André [11] attributed the typical soil odor to this species. Adams [12] appears to be the first author to determine actinomycetes to be responsible for taste and odor problems in soft waters after his observations made on Nile waters. Gerber and Lechevallier [13], Gerber [14] and Medsker et al. [15] identified the main metabolites of the actinomycetes (Figure 3). Rosen et al. [1] were the first researchers to succeed in isolating geosmin and 2-methylisoborneol from a natural water (Lake Ohio) by passing 3 m<sup>3</sup> of water through an activated carbon column and by extracting the activated carbon with chloroform, distillation, sulfuric ether and gas chromatography. Geosmin was found to be one of the components of the persistent musty, earthy odor of the actinomycetes. Collins et al. [16] isolated cadine-4-ene-1-ol from *Streptomyces odorifer*. Gerber [17] isolated selina-4(14)-7(11)-diene-9-ol from *Streptomyces fradiae*. Kikuchi et al. [18] obtained furfural from *Streptomyces filipinensis*.

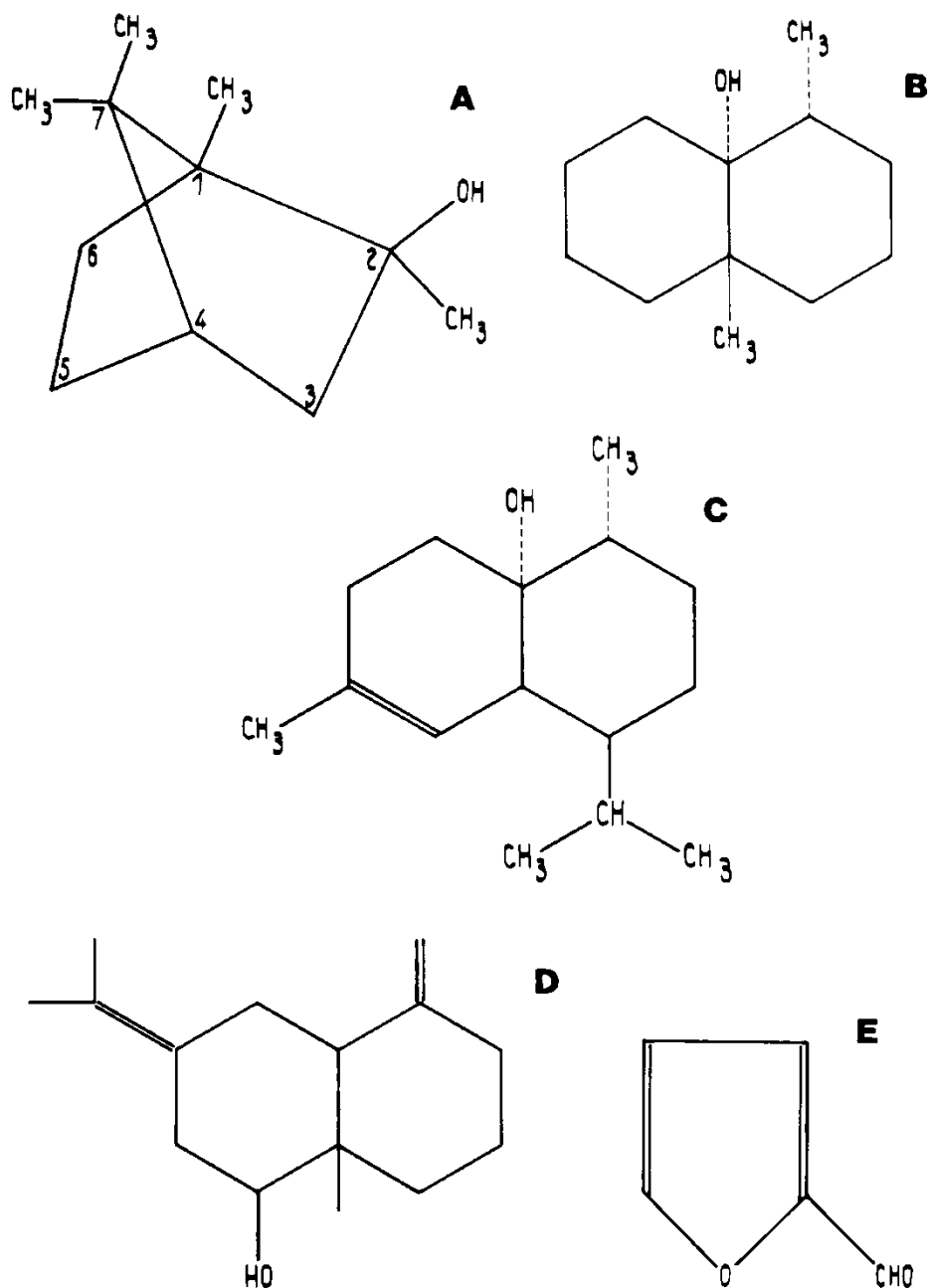
Most of the odorous substances mentioned above are sesquiterpenoids; these compounds generally are found in minute quantities in water. It has been assumed that they are derived via a biological pathway from the more common terpenoids after one or two functional groups have been lost (e.g., an isopropyl group).

### *Algae*

Algae also release metabolic substances that produce tastes and odors, especially during their growth phase. Palmer [19] arranged the main types of tastes and, especially, odors that could be found, according to the prevailing types of algae. He noted that variations in the nature of the odors depended on whether there was a moderate or large number of organisms in the medium. Some algae, the cyanophyceae in general, produce phenolated substances that may themselves be ill-smelling. When the water is disinfected with chlorine, chlorinated compounds may appear. They are very troublesome in producing a medicinal taste or odor (chlorophenols, although their concentration in the water is below the analytical detection threshold).

The most primitive algae can produce geosmin, as is the case for actinomycetes. Tabacheck and Yrkowski [20] noticed that cyanophyceae can

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**Figure 3.** Actinomycete metabolites that give a musty, silty or earthy taste to water. (A) Geosmin,  $C_{12}H_{22}O$ ; (B) methyl isoborneol,  $C_{11}H_{20}O$ ; (C) cudinene-4-ol-1; (D) selinadiene-4(14)-7(11)-ol-9; (E) furfural.

also produce 2-methylisoborneol. Algae can produce many other ill-smelling metabolites, such as alcohols, esters, aldehydes, ketones, fatty acids, mercaptans and two volatile metabolites with a fish-like odor: *n*-hexanol and *n*-heptanal. Collins [21] clearly indicates that *Synura petersenii* essentially produces heptanal, which may be considered to be the compound responsible for the characteristic odor of this organism.

After their death, the decay of the algae generally leads to formation of tastes and odors that come either from the dead algae themselves or from the activity of the true bacteria and the actinomycetes that live on them. It is to be noted in particular that the microbial activity of the cyanophyceae on decaying water bloom can produce several odorous sulfur compounds, such as methylmercaptan, isobutylmercaptan, *n*-butylmercaptan, and dimethylsulfide. These volatile sulfur compounds also can be produced by the algae while living.

### *Other Organisms*

*Bacteria (other than actinomycetes)*. Iron bacteria can give tastes and odors to ground- and surface waters. Lin [8,9] reported that the sulfate-reducing bacteria (such as *Desulfovibrio desulfuricans*) lead to the production of H<sub>2</sub>S.

*Fungi*. Collins [21] indicated that a mold (*Trichoderma viride*) synthesized a volatile and odorant metabolite, which he identified as being 6-pentylpyrone (C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>).

*Zooplankton*. Chang et al. [22] indicated that the nematodes and amoebae were liable to cause tastes and odors. They reported having found an oily substance with an earth and moldy odor from a culture of nematodes. Lin [8,9] also mentioned the crustacean *Entomostraca* (cyclops, daphnia) and *Keratella rotifera*. *Entomostraca*, in particular, would give a fishy taste to the water if they were too numerous.

### *Taste and Odor of Industrial or Agricultural Origin*

More than two million organic molecules are known throughout the world, and several thousands of new molecules are synthesized every year. Unchecked industrial or agricultural wastes contribute to the development of tastes and odors in water. The development of analytical

## Other Compounds

Rosen et al. [24] demonstrated the presence of 11 organic compounds in the water of the River Kanawha, Virginia: naphthalene, tetralin, styrene, acetophenone, ethylbenzene, *bis*-(2-chloroisopropyl) ether, diisobutylcarbinol, phenylmethylcarbinol, 2-methyl-5-ethyl pyridine, *bis*-(2-chloroethyl) ether and 2-ethylhexanol. Ten of these were in the neutral fraction. The resulting odor was greater than that contributed by any one component and even greater than the sum of all compounds; this potentiation of individual odor was ascribed to odor synergism. Koppe [25] isolated some sesquiterpenes in the Rhine that are supposed to be

## TASTE AND ODOR CONTROL 39

Table II. Odor Thresholds of Selected Phenolic Compounds

Substance	Threshold Concentration ( $\mu\text{g/l}$ )
Phenol	10,000
<i>o</i> -Cresol	71
<i>m</i> -Cresol	333
<i>p</i> -Cresol	45.5
2,4-Dimethylphenol	55.5
2,5-Dimethylphenol	33
3,4-Dimethylphenol	5,000
<i>o</i> -Chlorophenol	333
<i>m</i> -Chlorophenol	0.33
<i>p</i> -Chlorophenol	33
2,4-Dichlorophenol	0.65
2,5-Dichlorophenol	3.3
2,4,5-Trichlorophenol	11
2,4,6-Trichlorophenol	100
2,3,4,6-Tetrachlorophenol	915
Pentachlorophenol	857
1-Naphthol	500
2-Naphthol	3,333
Guaiacol	2

responsible for the bad odor of the Rhine water after bank filtration. Kölle et al. [26] separated odorous substances whose empirical formulas are  $\text{C}_{10}\text{H}_{14}\text{Cl}_2$ ,  $\text{C}_{10}\text{H}_{18}\text{Cl}_2$  and  $\text{C}_{10}\text{H}_9\text{Cl}_3$ . These odors resemble those of terpenes or chlorinated hydrocarbons.

The oil fraction is analytically divided into four classes:

1. volatile and immediately oxidizable, such as ethanediol;
2. volatile but not immediately oxidizable, such as cyclohexane;
3. slightly volatile and immediately oxidizable, such as phenol; and
4. slightly volatile but not immediately oxidizable, such as acetic acid.

The compounds in class 4 are the ones that may cause the greatest problems, since neither ozone nor permanganate oxidize them. These compounds are difficult to oxidize, and only activated carbon can eliminate them.

Cees et al. [27] indicated that naphthalene, 2-methylbenzothiazole and, particularly, chlorinated compounds, such as *bis*-(2-chloroisopropyl) ether, orthochlorophenol, dichlorobenzene and hexachlorobutadiene, are responsible for the taste of the River Rhine water. Compounds such

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as *o*-chlorophenol and *bis*-(2-chloroisopropyl) ether are also found in drinking waters at levels 100 times lower, which, however, are still high enough to cause odor problems for some of the population. Hydrocarbon concentrations of about 1 mg/l make the water unfit for human consumption. Mineral additives added to benzines lower the taste threshold notably. Cees and Zoeteman [28] found oil, substituted alkybenzenes and double-ring aromatic hydrocarbons in water; they considered them responsible for the unpleasant tastes.

### Pesticides

Increasing use of pesticides leads to the presence of minute traces of pesticide residues in water after leaching through soil. They give the water an unpleasant, moldy, slimy, or bitter taste (Table III). Hydrolysis of certain herbicides (Linuron, Monuron) produces aniline and aromatic compounds which cause bad tastes in water.

Table III. Taste Thresholds for Pesticides

Compounds	Taste Threshold (mg/l)	Characteristics of the Taste
Hexachlorobenzene	0.00013	Moldy, silty, bitter
Paradichlorobenzene	0.006	Moldy, silty
Chlordane	0.0025	
Lindane ( $\gamma$ -BHC)	0.002	
Endrin	0.0018	
Hexachlorocyclohexane ( $\alpha$ -BHC)	0.02	
DDT	0.02	
Malathion	0.05	Moldy
Parathion	0.003	
Methylparathion	0.02	
Thiophas	0.003	
Thiometon	0.001	
Chlorphos	0.05	
Toxaphene	0.005	
2,4-D	0.01	Moldy, silty
Methyldichlorocarbamate	0.02	Bitter, moldy



## **CHAPTER 4**

# **REMOVAL OF COLOR FROM DRINKING WATER WITH OZONE**

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Colored waters occur widely in nature, and they raise many problems when used for domestic or industrial purposes. It is now known that the color of waters comes mainly from the presence of humic substances in the water. These substances arise from decomposition of plant material, either in the ground or directly in the water. The color intensity of these waters depends on the nature and quantity of materials undergoing decomposition. The following factors affect the color of the waters:

1. contact time with the materials undergoing decomposition;
2. temperature (in tropical and subtropical countries, the decomposition process is very fast);
3. pH of the water.

In some cases, the color also can have seasonal causes: rapid growths of larvae and algae appear, giving the water a temporary color.

### **COMPOSITION OF COLOR-CAUSING SUBSTANCES**

Shapiro [1] demonstrated the similarity between colored substances and aqueous extracts of the soils. Investigations by Black and Christman [2] and Christman and Ghassemi [3] demonstrated that products from

## **COLOR REMOVAL**

Hall and Packham [9] showed that colored substances can be removed easily by various mineral coagulants, such as aluminum sulfate, ferric chloride and basic aluminum chloride. Treatment by reduction of the zeta potential to zero is not enough to remove all the color. Color removal becomes all the more efficient as the pH is lowered; pH 5.5 is the optimum value for color removal using aluminum sulfate. The polyhydroxyaromatic and carboxylic structures of colored organic by-products render them susceptible to the action of oxidizing agents. Chlorine, chlorine dioxide and ozone destroy the conjugated double bonds present in chromophores that generate color.

Black and Christman [2] introduced chlorine, chlorine dioxide and ozone into six types of strongly colored waters. The gas was supplied until a constant residual color value was obtained (Table I). It is apparent from this table that ozone was more effective than chlorine dioxide or chlorine for removing organic color. Both chlorine and chlorine dioxide produced their maximum effects within a contact time of 5–10 min., whereas ozone generally required 20–60 min. This is probably caused by the relatively low concentrations of ozone used. It can also be noted that color removal with ozone or any other oxidizing agent is not performed totally by oxidation of organic matter into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

## **Interference of Iron and Manganese**

Some colored waters may contain iron and manganese chelated with organic matter. Richard and Blue [10] noted that treatment with ozone may result in a degradation of the color in water through oxidation of the iron and manganese, which precipitate in the form of insoluble oxides. Excess ozone, however, may convert the uncolored  $\text{Mn}^{2+}$  ion into the soluble permanganate ion ( $\text{Mn}^{7+}$ ) of a pink color. The insoluble iron and manganese oxides are removed after ozonation, by rapid filtration.

**Tabella 6.3**

Costanti di velocità di reazione di alcheni sostituiti con ozono

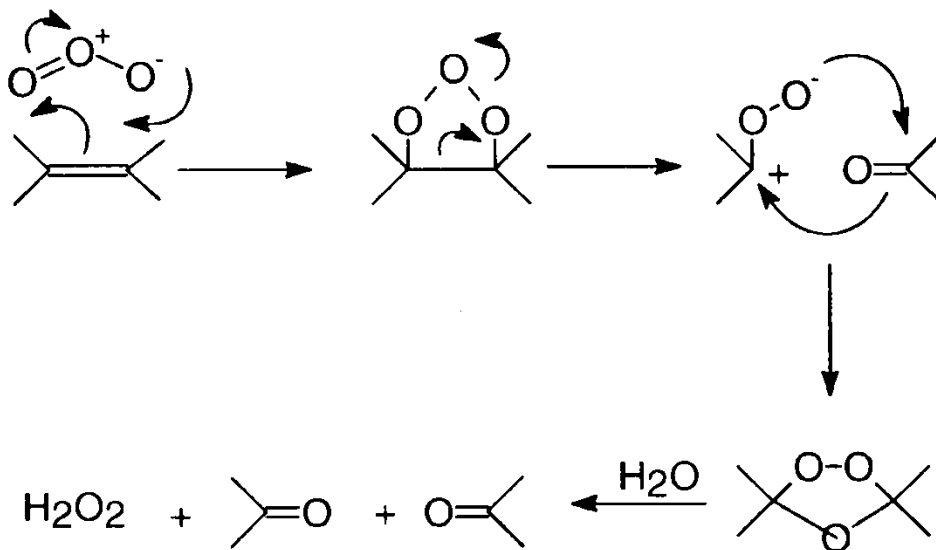
<i>Soluto</i>	<i>Concentrazione</i> $10^3 \text{ mol L}^{-1}$	<i>pH</i>	$k_{O_3}$ $\text{mol L}^{-1} \text{ s}^{-1}$
tetracloroetilene	0,7	2	< 0,1
tricloroetilene	0,06-0,6	2	$17 \pm 4$
cis-dicloroetilene	0,06-0,2	2	<800
trans-dicloroetilene	0,03-0,1	2	5700
1,1-dicloroetilene	0,04-0,4	2	$110 \pm 20$
acido maleico	0,1-0,7	2	1000
acido fumarico	0,1-1	2	6000
es-1-en-3-olo	$3 \times 10^{-3}$	2	100.000
es-1-en-4-olo	$3 \times 10^{-3}$	2	180.000
vinilbenzene	$7 \times 10^{-3}$	2-6	300.000
allilbenzene	$3 \times 10^{-3}$	2	120.000

L'ozono è un elettrofilo e reagisce quindi facilmente con composti che contengono nuvole  $\pi$ . La reattività è tanto maggiore quanto minore è il numero di atomi di cloro presenti sull'alchene, perchè questi atomi sono elettronattrattori e disperdono la nuvola elettronica  $\pi$  del doppio legame. Si nota una forte differenza tra alcheni cis e trans: il trans è più reattivo.

Che l'ozono sia un elettrofilo si nota anche considerando che l'ozonolisi degli alcheni in soluzione è una reazione periciclica che è favorita in alcheni ricchi di elettroni): lo stadio lento forma un ozonuro molare che si frammenta in un composto carbonilico ed un carbonilossido. Questi poi si ricombinano a dare l'ozonuro che infine si rompe a dare due composti carbonilici e perossido di idrogeno.

L'ozonizzazione delle acque sotterranee o di superficie contaminate da cloroalcheni è una pratica per la potabilizzazione che sta prendendo il sopravvento rispetto alla tecnica tradizionale, che usa il cloro. Infatti, la produzione di cloroorganici durante la clorazione dell'acqua rappresenta un pericolo concreto. Non si può tuttavia affermare che l'ozonizzazione dell'acqua non formi alcun composto tossico. Infatti è noto che lo ione bromuro  $\text{Br}^-$  è trasformato in bromato  $\text{BrO}_3^-$ , tossico, che deve quindi essere rimosso.

Nella tabella 6.4 sono riportate, sempre a pH acido, le velocità di reazione con ozono di benzeni sostituiti.



In questa tabella si possono individuare degli andamenti, la cui lettura sarebbe più facile se utilizzassimo una correlazione di Hammett. Ad esempio, consideriamo il benzene: ha una costante di velocità di 2; mentre il nitrobenzene, in cui il nucleo benzenico porta un sostituito elettronattrattore, ha una  $k = 0,1$ . Quindi, un sostituito elettronattrattore fa diminuire la velocità di reazione. L'anisolo, in cui il nucleo benzenico è legato ad un sostituito elettron-donatore come il gruppo metossile ha una  $k = 290$ , quindi una reazione più veloce; il clorobenzene ha una  $k = 0,75$  ossia è meno reattivo del benzene, ma più reattivo del nitrobenzene. Infatti il cloro ha una caratteristica di elettronattrattore inferiore al nitrogruppo.

Consideriamo adesso il fenolo: possiamo prevedere che quando sul nucleo fenolico sono presenti gruppi elettronattrattori la reattività diminuirà e quando sono presenti gruppi elettron-donatori la reattività aumenterà. Questa previsione è confermata dai dati in tabella, infatti il clorofenolo ha  $k = 600$ , il fenolo ha  $k = 1300$  ed il resorcinolo (1,3-difenolo) ha  $k > 300.000$ .

Da tutto ciò emerge che la reazione con  $\text{O}_3$  è favorita da gruppi elettron-donatori, come aspettato per un attacco elettrofilo dell'ozono sulla nuvola  $\pi$  dell'aromatico. Non sono disponibili con precisione ulteriori dettagli meccanicistici.

Se si misura la velocità di ozonizzazione di benzeni sostituiti rispetto a quella del benzene stesso: il rapporto  $\log k_{\text{aromatico}} / \log k_{\text{benzene}}$  può essere messo in relazione con l'effetto elettronico del sostituito in una correlazione di Hammett. Nella figura 6.5 l'effetto del sostituito è descritto dal  $\sigma^+$  di Brown. Questo indice descrive l'effetto elettronico generato dalla somma dell'effetto induttivo e dell'effetto mesomero. Quando il  $\sigma^+$  differisce di poco dal  $\sigma$ , ciò vuole dire che l'effetto induttivo prevale su quello mesomero. Nel caso di alcuni sostituiti come  $-\text{OH}$  o  $-\text{OCH}_3$ , il  $\sigma^+$  è molto diverso dal  $\sigma$ . Ciò vuole dire che in tali casi l'effetto mesomero è più importante di quello induttivo.

**Tabella 6.4**

Costanti di velocità di reazione di composti aromatici con ozono

<i>Soluto</i>	<i>Concentrazione</i> $10^3 \text{ moli L}^{-1}$	<i>pH</i>	<i>k</i> $\text{moli L}^{-1} \text{ s}^{-1}$
nitrobenzene	5/10	1	$0,09 \pm 0,02$
ione benzenesolfonato	10-800	1,7-2	$0,23 \pm 0,05$
1,2,4-triclorobenzene	0,05	2	$< 1,6$
1,4-diclorobenzene	0,05	2	$< 3$
clorobenzene	0,8-3	2	$0,75 \pm 0,2$
benzoato di metile	1000	2	$1,1 \pm 0,3$
ione benzoato	10-100	5	$1,2 \pm 0,2$
benzene	1-10	1,7-3	$1 \pm 0,4$
benzaldeide	2-10	1,7	$1,5 \pm 0,5$
isopropilbenzene	0,14	2.	$11 \pm 3$
toluene	0,4-4	1,7	$14 \pm 3$
4-nitrofenolo	0,01-14	1,7	$< 50$
etilbenzene	0,25-1	2	$14 \pm 3$
orto-xilene	0,03-0,8	1,7-5	$90 \pm 20$
meta-xilene	0,2-0,5	2	$94 \pm 20$
para-xilene	0,2-0,5	2	$140 \pm 30$
anisolo	0,05-0,8	2	$290 \pm 50$
1,2,3-trimetilbenzene	0,06-0,2	1,7	$400 \pm 100$
1,3,5-trimetilbenzene	0,05-0,1	1,7	$700 \pm 200$
4-clorofenolo	0,1-0,5	2	$600 \pm 100$
fenolo	0,01-0,1	1,7-2	$1300 \pm 300$
acido salicilico	0,1-1	1,3-3	$< 600$
ione salicilato	0.03	4-7	$3000 \pm 1000$
resorcinolo	0,003	2	$> 300.000$
naftalene	0,002-0,14	2	$3000 \pm 600$

La sensibilità di questa reazione all'effetto polare, cioè il  $\rho$  della reazione è di circa -4, un valore simile a quello delle reazioni che formano carbocationi. Ciò conferma che l'ozono si comporta da reattivo marcatamente elettrofilo.

Nella figura 6.6 è mostrata un'analogia correlazione di Hammett nella reazione di ozonizzazione di fenoli sostituiti in funzione del  $\sigma$  di Hammett. La sensibilità della re-

azione all'effetto polare (descritta dal  $\rho$ ) è -8.2, molto simile a quelle notate nelle reazioni che coinvolgono carbocationi.

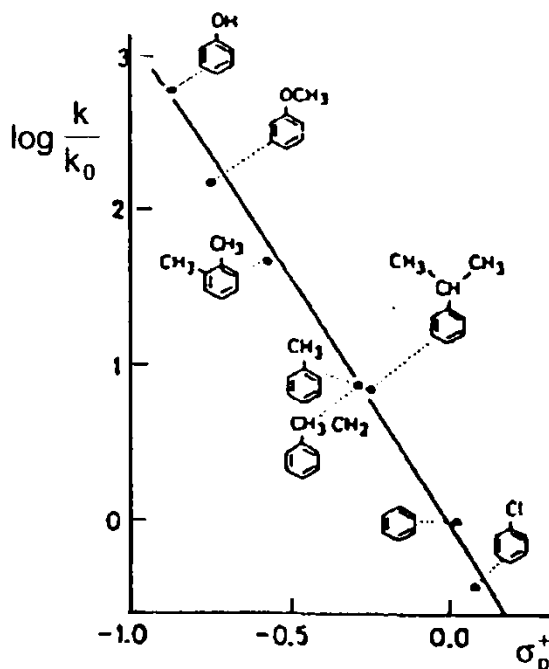


Figura 6.5. Relazione tra costanti di velocità di reazione di alcuni aromatici con ozono e valore della costante  $\sigma^+$  di Brown

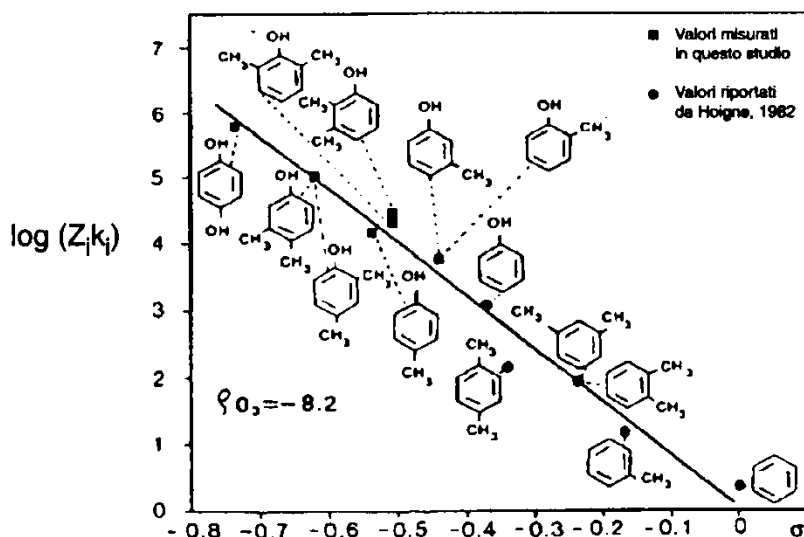
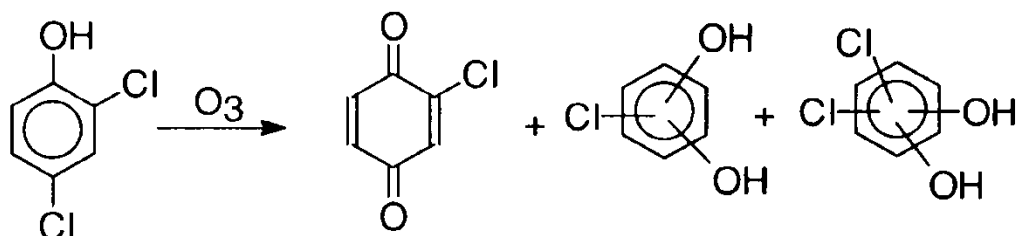
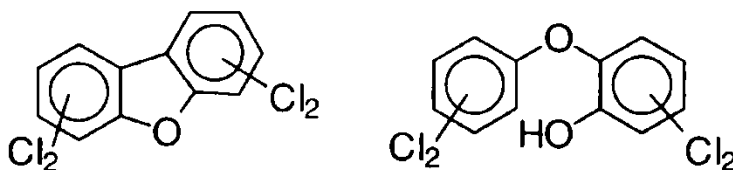


Figura 6.6. Relazione tra costanti di velocità di reazione di alcuni fenoli con ozono e valore della costante  $\sigma$  di Hammett

Per ciò che riguarda i prodotti di reazione ottenuti ozonizzando composti aromatici, si può osservare che l'ozonizzazione del 2,4-diclorofenolo forma cloroparabenzochinone, cloro e diclorodifenoli:



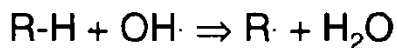
Si formano anche prodotti di polimerizzazione, derivanti da dimeri del tipo:



Quando l'ozono reagisce a pH neutro o alcalino, esso è rapidamente convertito in radicale ossidrilico  $\text{OH}\cdot$  attraverso le reazioni:

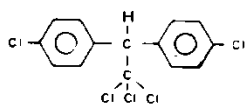


Il radicale ossidrilico reagirà quindi con i composti organici attraverso l'estrazione di un atomo di idrogeno. Il radicale organico così formato reagirà ulteriormente con l'ossigeno dando radicali perossidrilici che si frammenteranno ai prodotti finali.

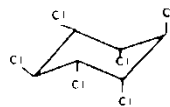


## EFFECT OF OZONE ON CHLORINATED ORGANIC COMPOUNDS

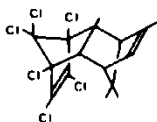
The main organochlorine pesticides are:



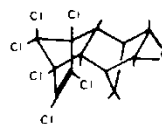
DDT



LINDANE



ALDRIN



DIELDRIN

### Treatment Applied

Pesticide	Treatment Applied				
	Oxidation by $\text{KMnO}_4$	Chlorination	Ozonation	Filtration Through Activated Carbon	Flocculation
Aldrin	a	a	a	a	b
<i>p,p'</i> -DDD	c	d	d	a	b
<i>o,p'</i> -DDT	c	d	d	a	b
<i>p,p'</i> -DDT	c	d	d	a	b
Dieldrin	d	d	d	a	b
Dimethoate	d	a	c	a	d
Diuron	d	b	c	a	d
Heptachlor	a	b	a	a	b
Heptachlorepoxyde	d	d	d	a	b
$\alpha$ -BHC	d	d	d	a	d
$\gamma$ -BHC	d	d	d	a	d
Linuron	d	b	c	a	d
Malathion	d	a	c	a	d
Methoxychlor	c	d	d	a	b
Polychlorinated Biphenyl (PCB)	d	d	d	a	b
Telodrin	d	d	d	a	b
Tetrachlorbenzol	d	d	d	a	b
Thiodane	c	b	d	a	b

<sup>a</sup> Good removal (>80%).

<sup>b</sup> Removal possible under better conditions.

<sup>c</sup> Poor removal (<80%).

<sup>d</sup> No removal.



Erb [11] et al. followed the oxidation of a solution containing mg/l of Lindane,  $\alpha$ -BHC, Heptachlor, Aldrin and HCB by 0.75 mg  $O_3$ /l-min for 12 min. After 3 min, all of the pesticides were still present at 100%; after 6 min, 100% Aldrin and  $\alpha$ -BHC were present and 91% Lindane, 75% HCB and 95% Heptachlor still were left. After 12 min, removal percentages reached 96% for Aldrin, 80% for Heptachlor and Lindane, 70% for  $\alpha$ -BHC and 50% for HCB. Prengle and Mauk [12] reported that ozonation of DDT in water takes place very slowly, but that the oxidation rate is higher when ozone and ultraviolet (UV) radiation are combined (Figure 2).

Gäb [13] reported that:

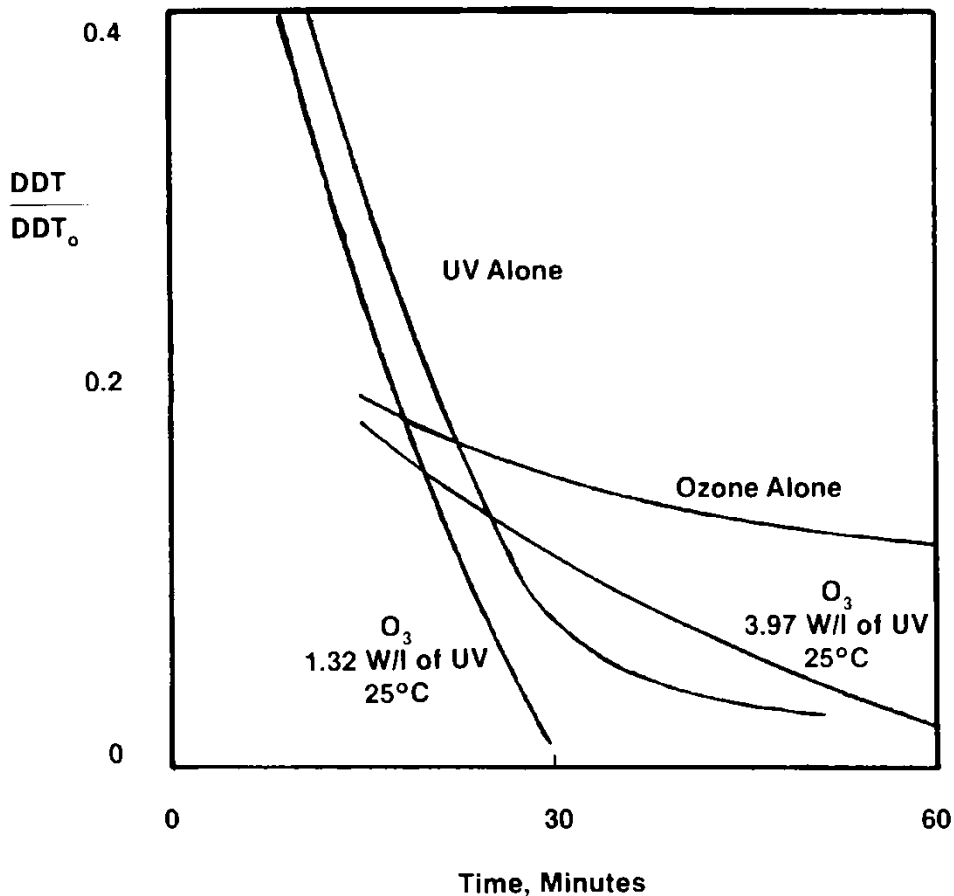
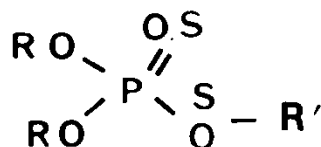


Figure 2. Destruction of DDT by ozone and ultraviolet.

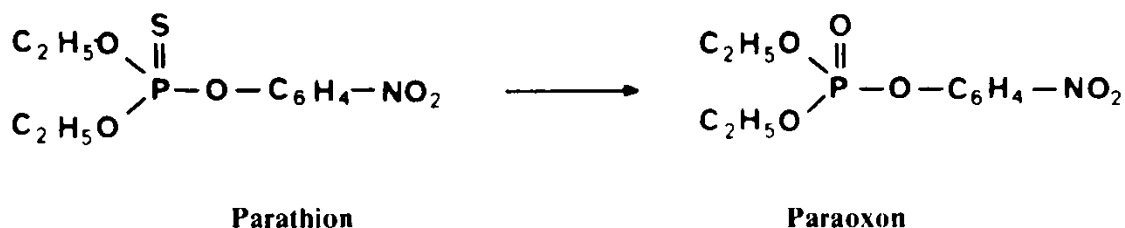
## OZONATION OF ORGANOPHOSPHORUS PESTICIDES

Organophosphorus insecticides are generally less stable in water, but some are highly toxic. They have the following general formula:



Gabovič and Kurennoj [14] were the first to show the effect of 10 mg/l of ozone on Parathion, methyl Parathion and trichlormephos in removing the odor developed by these compounds. Gunther et al. [15] also showed that Parathion could be oxidized to Paraoxon.

Richard et al. [16] ozonated five organophosphorus pesticides by bubbling 0.1 liter/min of ozone air into 500 ml of solution. Maximum ozone generator production was 2 g/hr. The results are summarized in Table VII. Richard et al. [17] studied Parathion ozonation in a pilot column. These tests confirmed that Parathion may first convert into Paraoxon.



Removal of the Paraoxon formed requires introduction of a minimum ozone dose of 5 mg/l for an initial solution with an 80  $\mu\text{g/l}$  of Paraoxon content. It has also been shown that, in all cases, Parathion removal is faster in an acid medium, but Paraoxon disappears more rapidly in an alkaline medium.

Richard et al. [18] have shown by nuclear magnetic resonance analysis,

Table VII. Pesticide Remaining (%) after Ozonation of Several Organophosphorus Pesticides

Pesticide	Ozone Applied (mg/l)					
	0	1	2	3	4	5
Malathion	100	65	61	45	37	12
Parathion	87	67	58	41	20	15
Methyl Parathion	125	98	83	40	28	20
Fenitrothion	120	72	33	16	13	5
Ronnel	26	23	21	15	11	8

thin-layer chromatography and gas chromatography, that the first phase of Parathion ozonation is Paraoxon, the latter then being oxidized to 2,4-dinitrophenol and picric acid. An excess ozone dose leads to complete Parathion mineralization into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  (Figures 3 and 4).

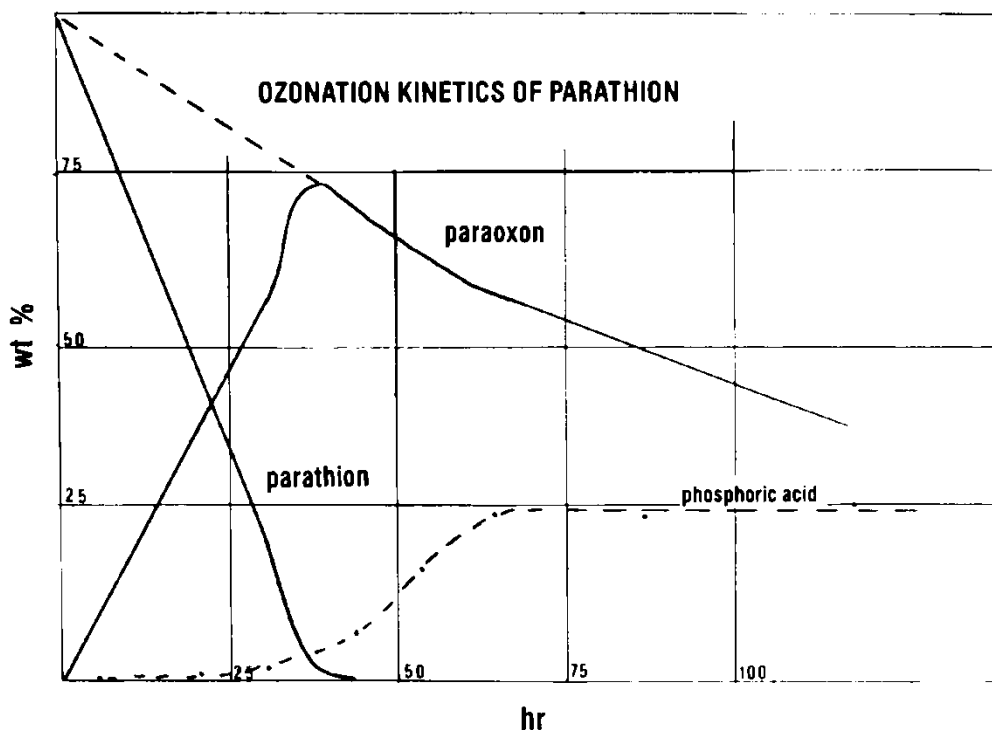


Figure 3. Curves of Parathion, Paraoxon and phosphoric acid oxidation by ozone. Ozonator airflow = 100 liter/hr; power = 50 W.

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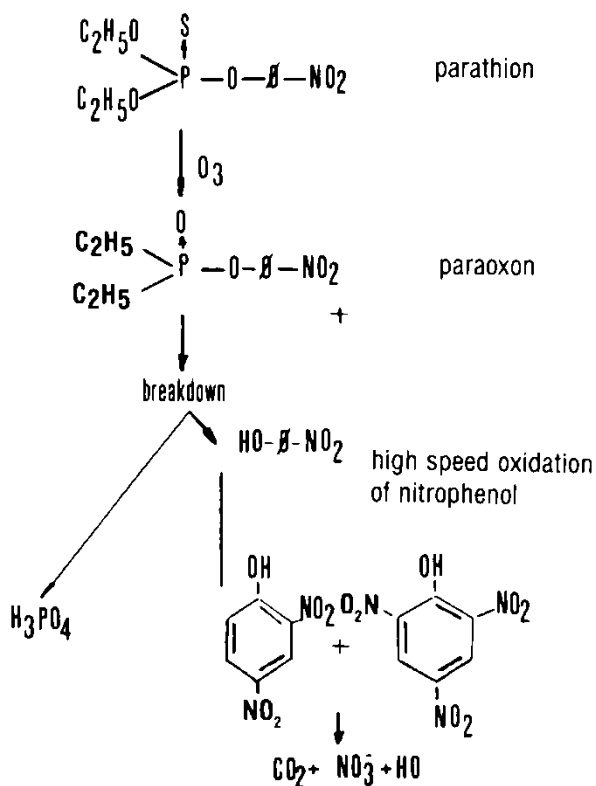
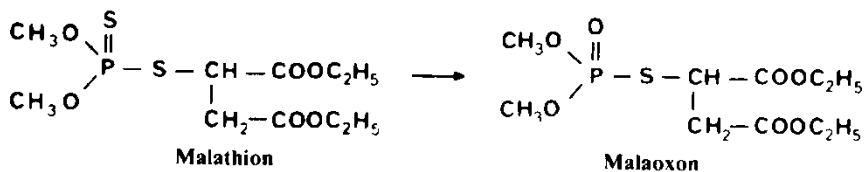
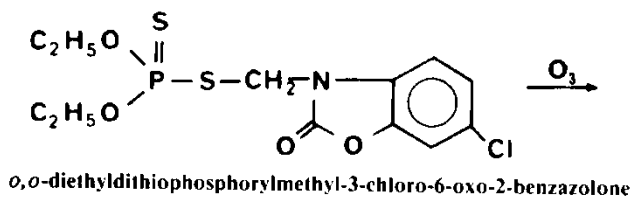


Figure 4. Ozonation of Parathion.

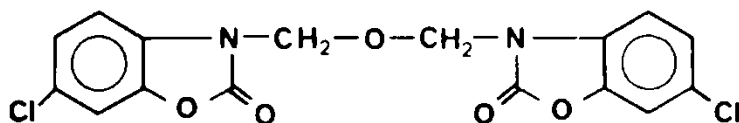
Richard and Bréner [19] ozonated Malathion and isolated Malaoxon as the first intermediate. If ozonation continues, Malaoxon is destroyed to  $\text{H}_3\text{PO}_4$  and unidentified substances:



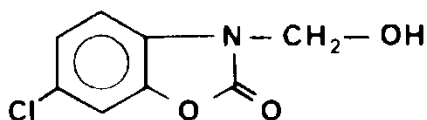
After ozonation, Phosalone does not produce an oxon derivative as this compound must be unstable:



Furthermore, two metabolites have been identified:

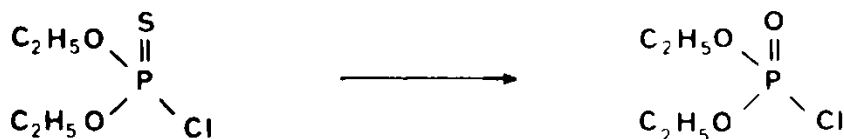


*bis*-(chloro-6-oxo-2-benzoxazolyl-3-methyl) ether

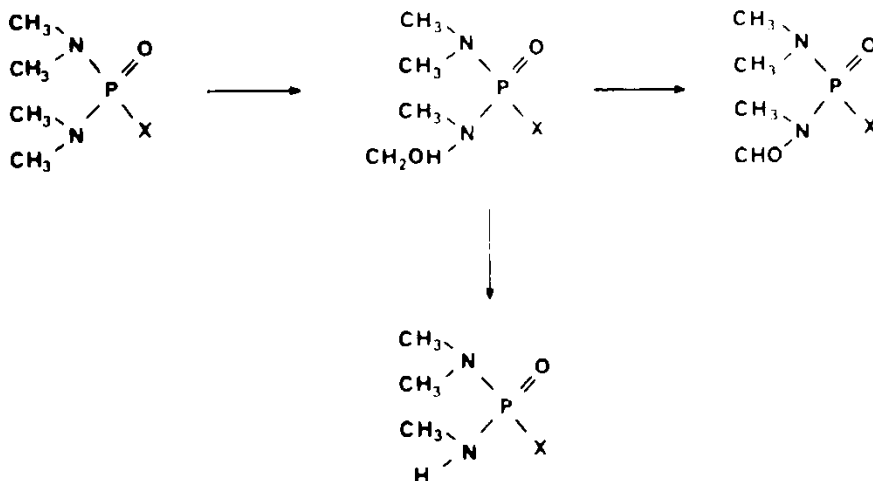


hydroxymethyl-3-chlorobenzoxazolone

Laplanche and Martin [20] ozonated chlorothiophosphate compounds. A first oxidation derivative is formed by substitution of the sulfur by oxygen:

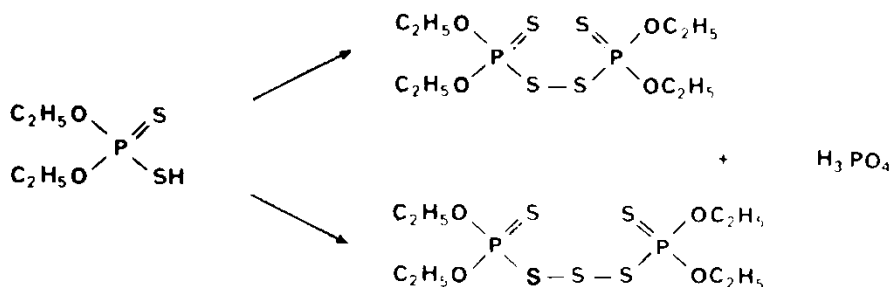


The oxon derivative of Parathion is more toxic than Parathion itself; in addition, certain metabolites of oxidation by ozone are stable. The authors [20] also showed that, in the presence of ozone, *bis*-dimethyl-amino-chlorophosphate causes substitution reactions on the dimethyl-amino group:

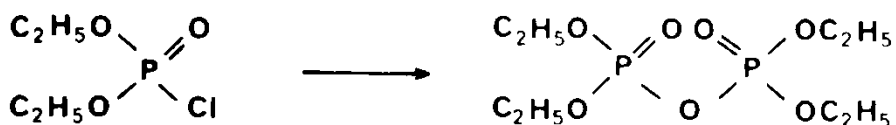


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Ozone causes cleavages in phosphorus compounds and leads to the formation of condensates. Thus, diethylthiophosphoric acid combines through a two- or three-sulfur-atom bridge:



The same holds true for diethylchlorophosphate, ozonation of which causes molecule dimerization:



Tetraethylpyrophosphate is a stable compound.

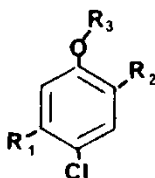
Laboratory tests conducted by Richard et al. [21] showed that Parathion ozonation kinetics are first-order with respect to Parathion and ozone. Block et al. [22] showed that the ozonation of a 123-mg/l Malathion solution for 120 min ensures reduction percentages of 10% for chemical oxygen demand, 20% for the total organic carbon and 12% for the chlorine demand. Neither the biochemical oxygen demand nor the biodegradability index are noticeably affected. Moreover, malathion is 95% removed.

## OZONATION OF PHENOXYALKYL ACIDS AND ESTERS

Table VIII shows the structural and line-formula designations of the main phenoxyalkyl acids utilized nowadays as defoliant. Weil et al. [23] ozonated 0.001 M solutions of 2,4,5-trichlorophenoxyacetic acid using, 0.048 mol/hr of ozone, and identified oxalic acid, glycolic acid, dichloromaleic acid, chloride ion and CO<sub>2</sub> as oxidation degradation products. They found no ozonides or preoxidized polymers. Chloromaleic acid concentration reached its maximum after 8 min of ozonation, glycolic acid after 12 min and oxalic acid after 20 min. The concentra-

Table VIII. Phenoxyalkyl Acids and Esters

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
2,4-D	H	Cl	-CH <sub>2</sub> COOH
2,4-DP	H	Cl	-CH(CH <sub>3</sub> )COOH
4-chloro-2-methylphenoxyacetic acid	H	CH <sub>3</sub>	-CH <sub>2</sub> COOH
4-chloro-2-methylphenoxybutyric acid	H	CH <sub>3</sub>	-CH(CH <sub>3</sub> )COOH
4-chloro-2-methylpropionic acid	H	CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH
2,4,5-T	Cl	Cl	-CH <sub>2</sub> COOH



tions of all intermediates decreased with increasing ozonation time. Dichloromaleic acid concentration tended toward zero after 25 min. The reaction mechanism is proposed in Figure 5.

Doré et al. studied 2,4-D and 4-chloro-2-methylphenoxyacetic acid (MCPA) ozonation with concentrations of  $2 \times 10^{-4}$  mol/l and showed that a 20-min period of ozonation was required for the molecule to lose its aromatic characteristic (opening of the benzene ring); an  $O_3/\phi-OH$  molar ratio of 5 was required to have the benzene ring opened by ozone. Table IX illustrates these results.

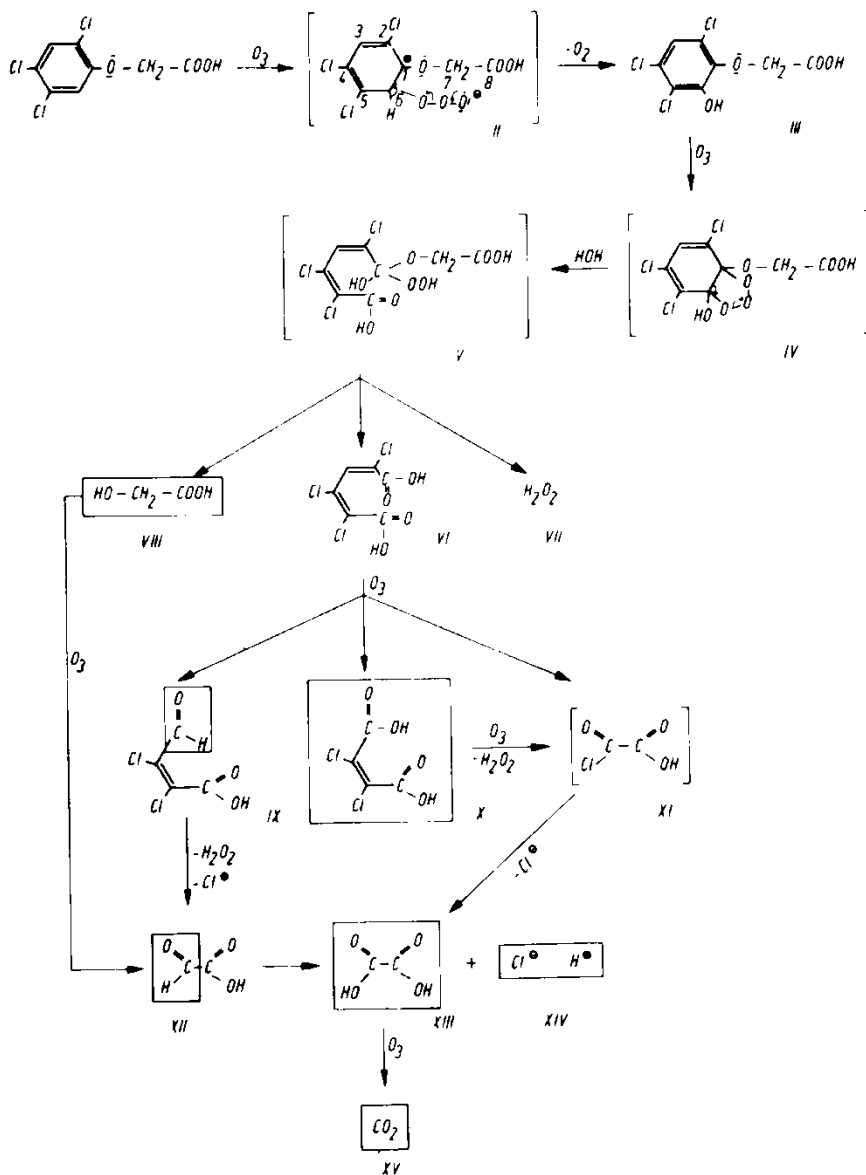
## OZONATION OF NITROGENOUS SUBSTANCES

Nitrogen pesticides (Table X) include compounds of the carbamate and atrazine families. Bauer [7] showed that two herbicides (Linuron and Dinuron) can be oxidized partially by ozone. No degradation products were found during the analysis. Erb et al. [11] showed that an applied ozone dose of 0.75 mg  $O_3$ /1-min for 6 min ensures 100% removal for Monuron and 50% for atrazine.

## NATURAL MEDIUM INTERFERENCE WITH PESTICIDE OZONATION

Mallevalle et al. [25] ozonated an Aldrin solution and found that this compound was easily degradable by ozone. Furthermore, when chelated

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**Figure 5.** Proposed mechanism of 2,4,5-trichlorophenoxyacetic acid ozonation [23].

Aldrin was added to a solution containing humic acids, 0.45 g/l of aldrin was detected after 10 min of ozonation. These researchers stated that study of ozonation in pure solutions may lead to erroneous conclusions about ozone doses to be applied, since humic acids chelate and protect pesticides.

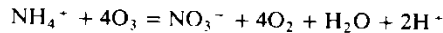


## OZONATION OF AMMONIA

Strecker and Thienemann [1] studied the action of ozone on liquid ammonia. They observed the formation of nitrite and nitrate, but ozone did not react readily in the aqueous phase. Papko [2] also showed that ammonia was easily oxidized to nitrate by ozone. However, the reaction was slower in water. Huibers et al. [3] did not observe variations in ammonia concentration when secondary effluent was ozonated at pH values between 7 and 8. Reduction in ammonia concentrations was high at pH 10.6, after caustic soda was added to the water. Singer and Zilli [4] showed that under normal ozone application conditions, no ammonia

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values  $>8.5$  (Figure 1). Under these conditions,  $\text{NH}_4^+$  oxidation to  $\text{NO}_3^-$  is complete (Figure 2):



The rate of  $\text{NH}_4^+$  ion removal seems to decrease with decreasing concentration. The half-life is independent of initial concentration; this suggests a first-order reaction with respect to ammonia nitrogen (Figure 3):

$$-\frac{d(\text{NH}_4^+)}{dt} = k(\text{NH}_4^+)$$

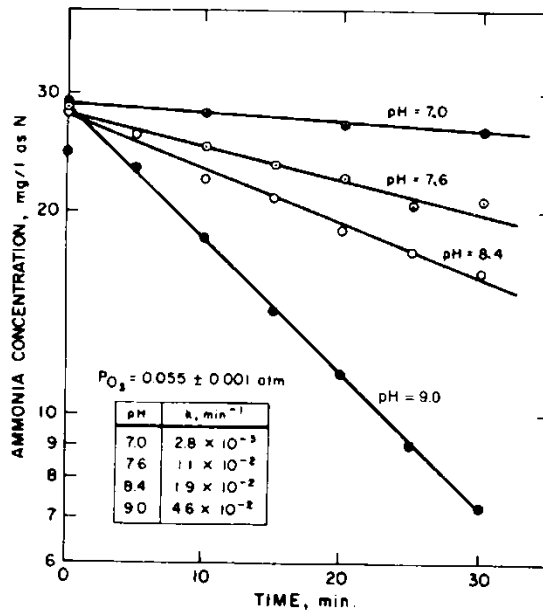
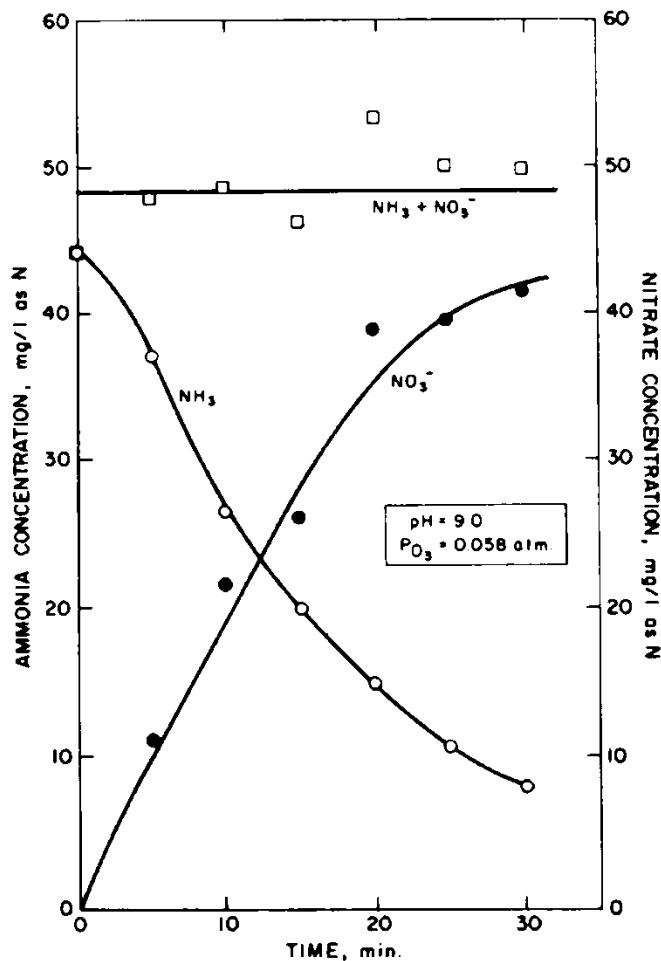


Figure 1. Effect of pH on rate of ammonia oxidation with ozone.

At temperature =  $20^\circ\text{C}$ , pH 9 and partial ozone pressure =  $0.056 \text{ atm}$ , the authors [4] found that the average value of the reaction rate constant under the stated conditions is  $5.2 \pm 0.3 \times 10^{-2}/\text{min}$ . At pH 9, the oxidation yield is 10-20 times higher than that obtained at pH 7. Stoichiometric ozone consumption is 4 moles of ozone per mole of ammonium ion. Molar ratios actually obtained are shown in Table I. This ratio (4



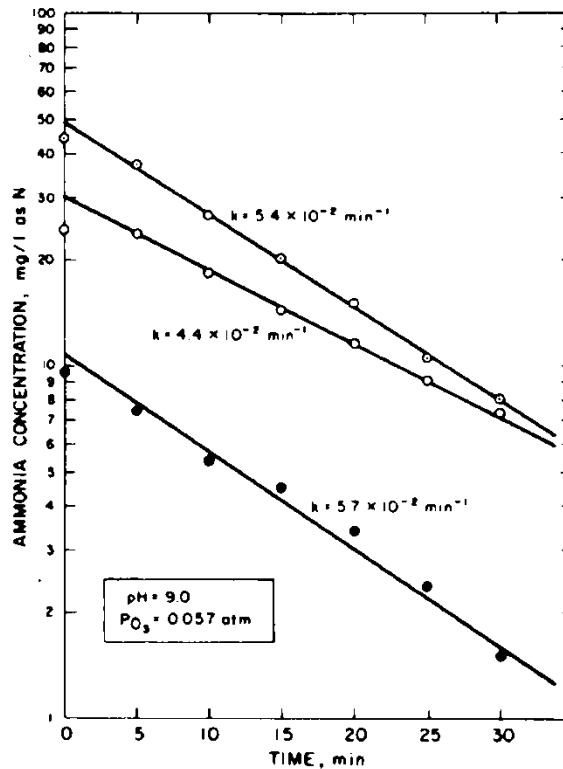
**Figure 2.** Ammonia removal and nitrate formation following ozonation of  $\text{NH}_4\text{Cl}$  solutions containing 50 mg/l ammonia, at pH 9.0.

$\text{mol O}_3/\text{mol NH}_4^+$ ) decreases as the pH increases, whereas the decomposition rate increases under the same conditions. Two hypotheses can be proposed:

1. ozone decomposition products react or
2. higher ozone reactivity at high pH makes for greater ozone losses.

The rate of reaction increases as the partial pressure of ozone increases up to a maximum of 0.049 atm (Figure 4).

In secondary effluents with a pH of 7, organic matter is oxidized before the ammonium ion (Figure 5). However, at pH 9,  $\text{NH}_4^+$  is oxidized before organic matter (Figure 6).



**Figure 3.** Conformance of ammonia oxidation to first-order kinetics at different initial concentrations of ammonia.

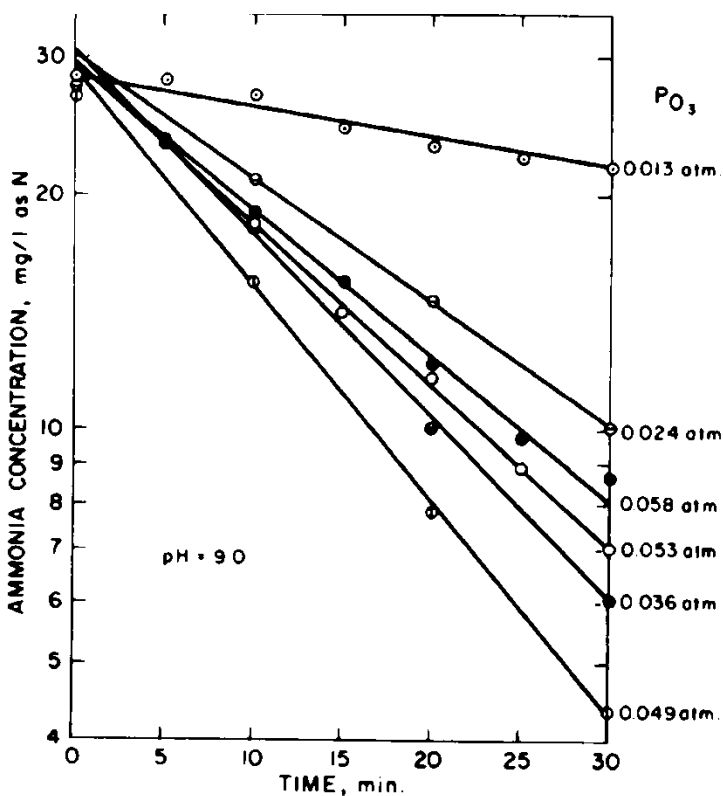
### Reaction Kinetics

Hoigné and Bader [5] explained ammonia ozonation kinetics by a direct reaction of molecular ozone and a radical-type reaction by means of  $\text{OH}^\cdot$  (Figure 7). Ozone oxidation of  $\text{NH}_3$  is only significant in the presence of high concentrations of  $\text{NH}_3$ , since  $\text{NH}_4^+$  cannot be oxidized, and free  $\text{NH}_3$  concentration thus depends closely on the pH (Figure 8). For pH values  $<9$ , it is mainly molecular ozone that initiates ammonia oxidation. In this pH range, only a very small proportion of ammonia is in the form of  $\text{NH}_3$ , and the rate constant of  $\text{NH}_3$  reacting with  $\text{O}_3$  is  $20.4/\text{M}^{-1} \text{sec}^{-1}$ . The oxidation reaction is thus weak. In the case of ozonation with a prolonged contact time, bicarbonate ions can improve ammonia oxidation by quenching part of the  $\text{OH}^\cdot$  radicals, which, otherwise, would speed up ozone decomposition (Figure 9). Decomposition of molecular ozone by reactions with free  $\text{NH}_3$  is linear (Figure 10).

For pH values  $>9$ , ozone decomposition into radicals occurs before

**Table I. Consumption of Ozone by Ammonium Chloride Solutions**

<b>Experiment No.</b>	<b>pH</b>	<b>Ozone Conc (vol %)</b>	<b>Cumulative Ozone Output (mg)</b>	<b>Ozone Collected in Final Trap (mg)</b>	<b>Ozone Consumed in Reactor (mg)</b>	<b>Initial Ammonia Conc (mg as N)</b>	<b>Final Ammonia Conc (mg as N)</b>	<b>Ammonia Oxidized (mg as N)</b>	<b>Molar Ratio of Ozone Consumed per Ammonia Oxidized</b>
1	7.0	5.4	3816.0	3031.0	785.0	29.0	26.5	2.5	91.9
2	7.6	5.5	3758.7	3199.2	559.5	28.3	21.0	7.3	22.4
3	8.4	5.6	3840.0	3196.2	643.8	28.0	16.3	11.7	16.1
4	9.0	5.3	3717.6	3007.7	709.9	24.4	7.3	17.1	12.1

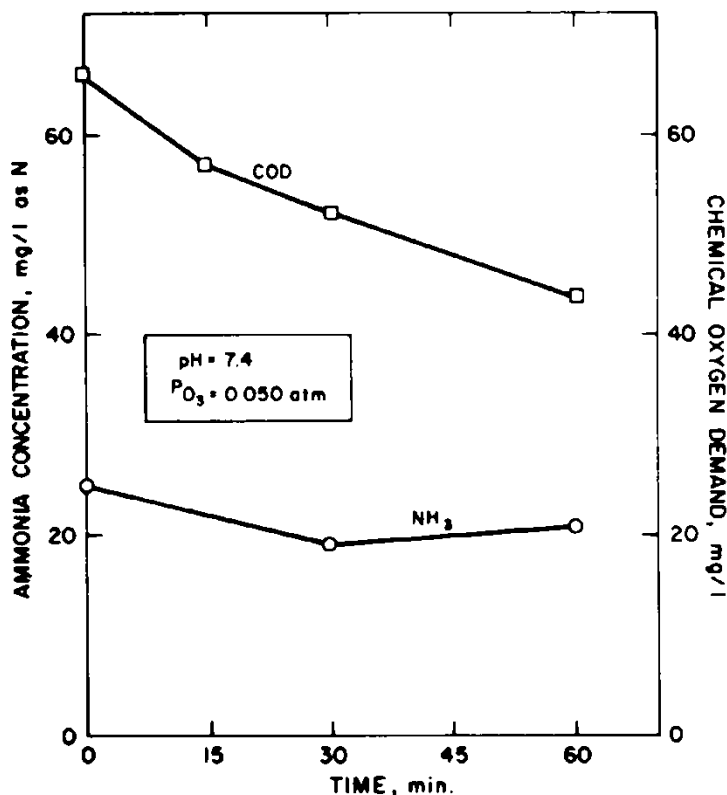


**Figure 4.** Effect of ozone partial pressure on kinetics of ammonia oxidation at pH 9.0.

oxidation of free  $\text{NH}_3$ . Only  $\text{OH}^\cdot$  radicals take part in initiating  $\text{NH}_3$  oxidation. The rate constant of  $\text{OH}^\cdot$  radical formation by gamma radiation is  $8.7 \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$ . This conforms with rates found during ammonia ozonation experiments.

Carbonate ions and other solutes (benzene, methanol,  $\text{H}_2\text{O}_2$ , etc.) consume  $\text{OH}^\cdot$  radicals and protect ammonia in fast reactions whose oxidation yield  $\Delta\text{NH}_3/\Delta\text{O}_3$  drops (Table II). For a surface water with a pH close to 8 and containing 1 mg/l of ammonia nitrogen ( $10^{-5} \text{ M}$  free  $\text{NH}_3$ ), it can be calculated that the rate of  $\text{OH}^\cdot$  radical consumption by  $\text{NH}_3$  would be  $8.7 \times 10^2/\text{sec}$ . Analysis shows that all of the other solutes present in the water of Lake Zürich scavenge  $\text{OH}^\cdot$  radicals 40 times faster ( $2 \times 10^4/\text{sec}$ ).

Ammonia can inhibit the oxidation of organic solutes present in a water that captures  $\text{OH}^\cdot$  radicals. The rate constant of  $\text{NH}_3$  capture of  $\text{OH}^\cdot$  radicals is low, compared to that of carbonate ions. The action of free  $\text{NH}_3$  will be perceptible when its concentration is of the same order

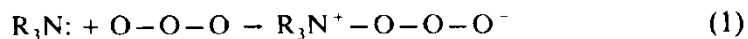


**Figure 5.** Ammonia oxidation and COD removal following ozonation of secondary effluent with no pH adjustment.

of magnitude as that of other solutes. Thus, as far as potable water is concerned, the protective effect of ammonia will be negligible.

### ACTION OF OZONE ON AMINES

Ross [6] showed that the conjugate acid of trimethylamine,  $(\text{CH}_3)_3\text{NH}_3^+$ , is much less susceptible to oxidation than trimethylamine itself. In a series of papers concerning ozone reactions with amines, Bailey and co-workers [7,8] proposed a working hypothesis that implies an initial electrophilic attack of ozone along with the formation of an amine-ozone adduct:



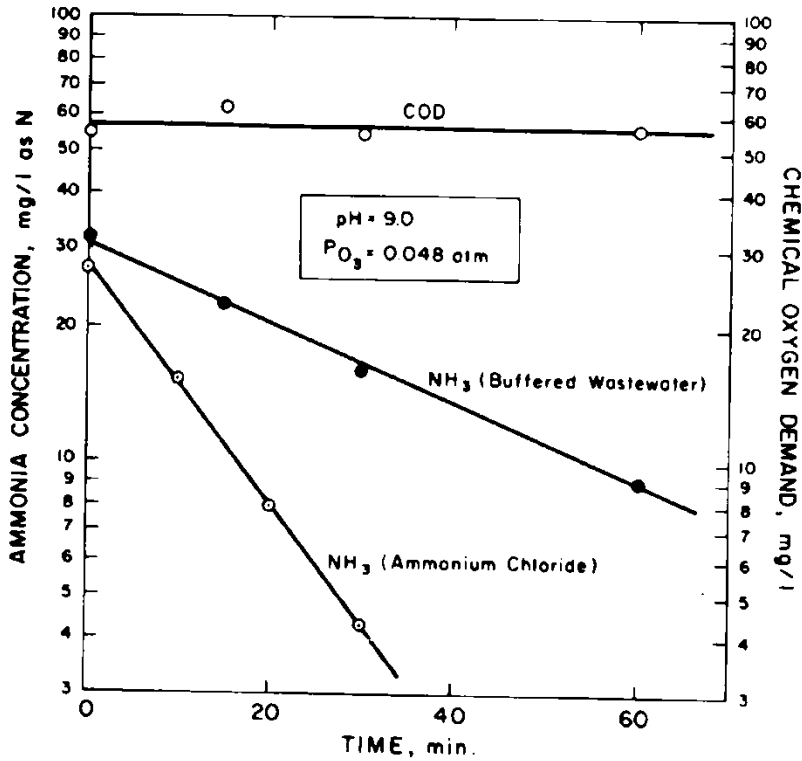


Figure 6. Ammonia oxidation and COD removal following ozonation of secondary effluent buffered at pH 9.0.

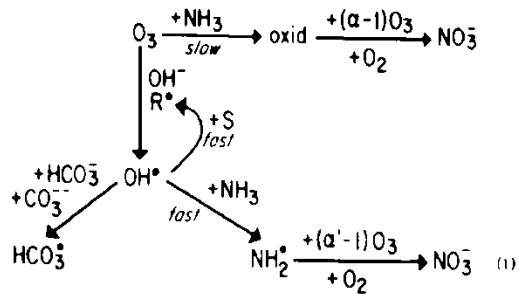
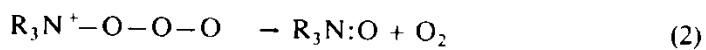
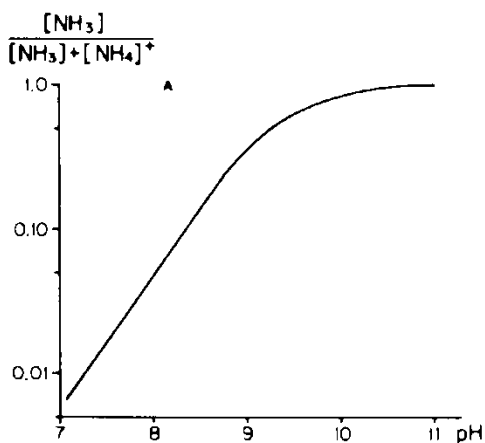


Figure 7. Mechanism of ammonia oxidation by ozone.

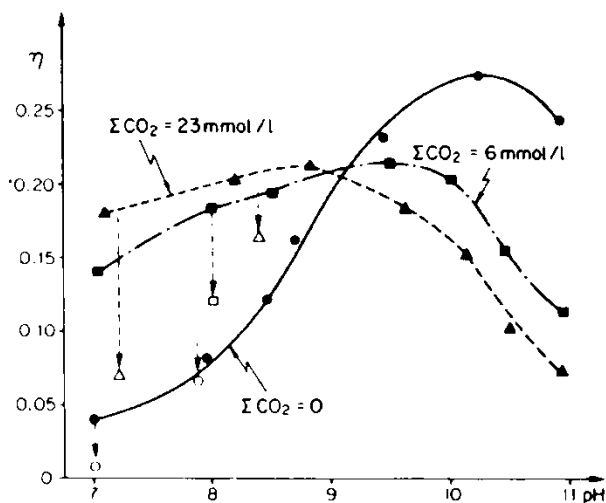
This adduct undergoes subsequent reactions:

1. loss of molecular oxygen with formation of an amine oxide or oxidation products in the presence of an excessive amount of ozone:



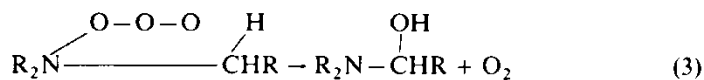


**Figure 8.** Relative amount of oxidizable free  $\text{NH}_3$  existing in equilibrium with  $\text{NH}_4^+$ . Calculated for  $\text{pK}_a = 9.27$  (ionic strength = 0.12).



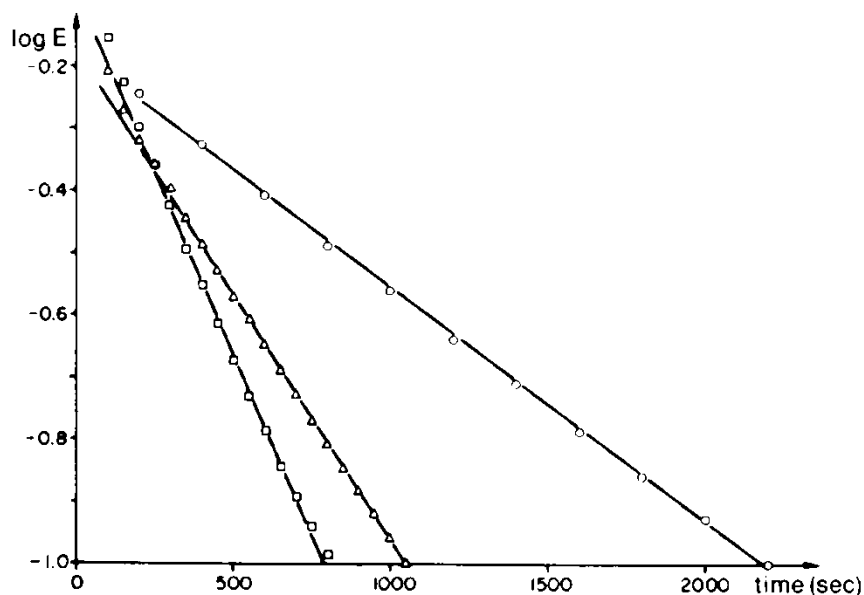
**Figure 9.** Yield of oxidation of  $\text{NH}_3$  to  $\text{NO}_3^-$  vs pH for different carbonate concentrations ( $\eta = -\Delta\text{NH}_3 / -\Delta\text{O}_3$ ; - - - - = yields measured when reaction was stopped after 15 min;  $[\text{NH}_4^+ + \text{NH}_3]_0 = 1.4 \text{ mM}$   $\Sigma\text{CO}_2$ :  $[\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}]$ ).

2. intramolecular oxidation of a side chain, which may give rise to molecular oxygen and substances from a tertiary amino alcohol:



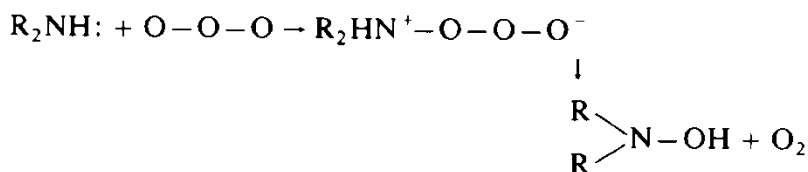


It should be noted that the preferential path varies with the oxidant, amine and solvent.



**Figure 10.** Consumption of ozone vs time for different concentrations of  $\text{NH}_3$  ( $[\text{O}_3]_0 \approx 0.3 \text{ mmol/l}$ ;  $[\text{HCO}_3^-] = 22 \text{ mM}$ ;  $\text{NH}_4\text{Cl}$  added:  $\square = 12 \text{ mM}$ , pH 7.6,  $\Delta = 6 \text{ mM}$ , pH 7.3,  $\circ = 3 \text{ mM}$ , pH 7.2;  $E = \text{UV extinction measured at } 258 \text{ nm}$ ).

Likewise, the reaction rate will be affected. The authors specify that the electrophilic attack of ozone on the nucleophilic site of amine nitrogen would be expected to be slow in an aqueous medium due to solvation for dimethylamine:



**Table II.** Yield of  $\text{NH}_3$  Oxidation in Water of Different Carbonate Hardnesses (pH 10.9)<sup>a</sup>

Type of Water	$\eta$ (%)	$\eta$ After $\text{CO}_3^{2-}$ Eliminated (%)
Double Distilled	$9 \pm 1$	$11 \pm 2$
Double Distilled + $0.8 \text{ mM CO}_3^{2-}$	6	12
Double Distilled + $4 \text{ mM CO}_3^{2-}$	1	11
40% Tap Water ( $2.5 \text{ mM CO}_3^{2-}$ )	2	8

<sup>a</sup>  $\eta = -\Delta\text{NH}_3 / -\Delta\text{O}_3$ ;  $[\text{NH}_3]_0 = 0.11 \text{ mM}$ ;  $[\text{O}_3]_0 = 0.31 \text{ mM}$ .

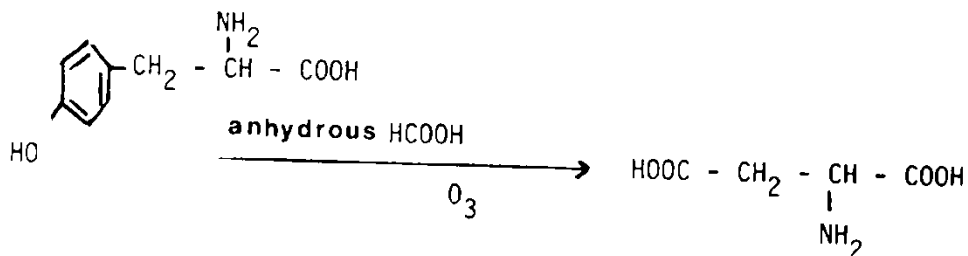
The mechanism of amine oxide formation is a first-order reaction with respect to amine and ozone concentrations. Rogozhkin [9] reported that dimethylamine can be removed from waste effluents using ozone in an alkaline medium. The resulting oxidation products are reported as formaldehyde, formic acid, carbonic acid, nitrites and nitrates. Neytzell-De Wilde [10] studied methylamine ozonation in waste effluents.  $\text{CH}_3$  groups affect reactivity of the  $-\text{N}$  site; thus, trimethylamine is oxidized more rapidly (Figure 11 and Table III). For pH values greater than 10, dimethylamine and trimethylamine removal is first order. Ozonation tests conducted on a solution of dimethylamine over pH range from 8 to 10 confirm the effect of pH (Figure 12, Table IV). The effect of pH, especially high pH values, on amine oxidation confirms that the conjugate acids of mono-, di- and trimethylamine (MMA, DMA and TMA, respectively) are less oxidizable than are the amines. Amine removal from water preferably is carried out in an alkaline medium.

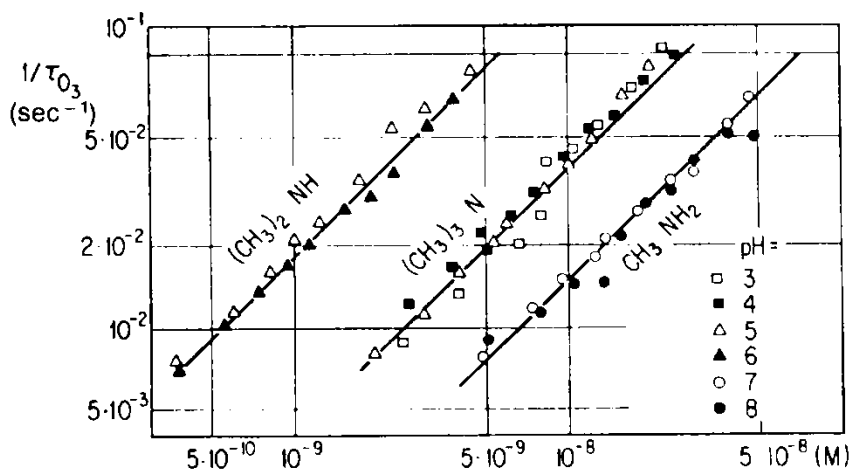
Hoigné and Bader [11] showed that direct ozone reaction of ammonia takes place at pH values  $< 8$ . The rate constant is low, since it is determined by free methylamine concentration ( $< 0.1\%$  of these amines are in the form of free amines in this pH range). The reaction is first order with respect to ozone and free amine concentration (Figure 13). Hoigné and Bader [11] also showed that lowering of trimethylamine concentration by 37% ( $1/e \times 100$ ) at pH 8 required 70 sec; this time was 600 sec for monomethylamine (Figure 14). Under identical oxidation conditions,  $10^5$  sec would be required for ammonia removal.

## AMINO ACID OZONATION

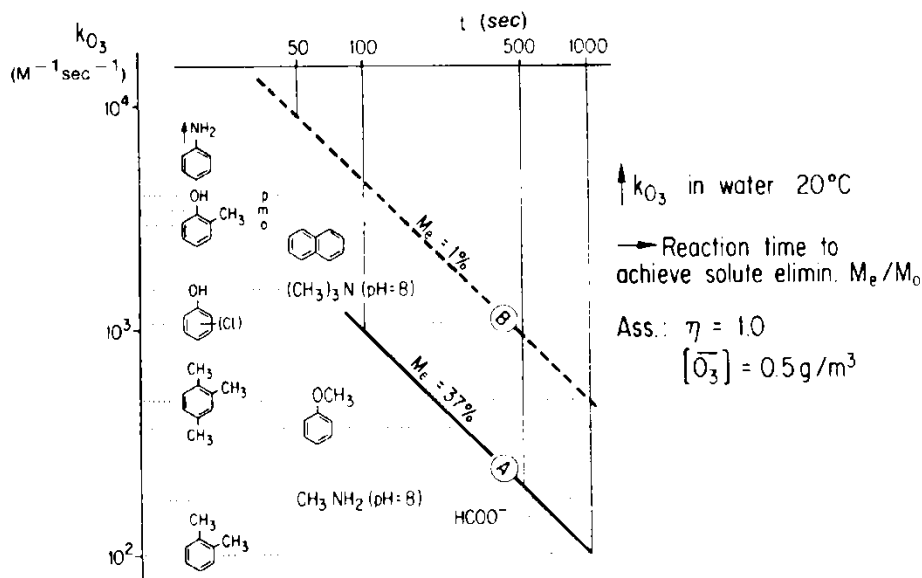
### Effect of Reaction Medium

The reaction medium has a considerable effect on the mechanism of amino acid oxidation by ozone. Mudd and Leavitt [12] showed that tyrosine oxidation in anhydrous formic acid causes the appearance of aspartic acid according to:





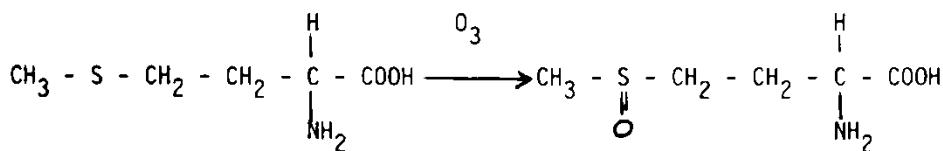
**Figure 13.** Direct ozone reaction with methylamines (free amine) calculated from  $[ ]_{tot}$  and  $CH_3NH_3^+$   $pK_a = 10.7$ ;  $(CH_3)_2NH_2^+$   $pK_a = 11.0$ ;  $(CH_3)_3NH^+$   $pK_a = 9.9$ .



**Figure 14.** Direct ozone reaction.

### Methionine Ozonation

Methionine is very easily ozonated. As previously seen, this is due to the reactivity of the SH group. The sole product identified is methionine sulfoxide, which is not oxidized to methionine sulfone (Figure 15A).



**Table V. Absorption of Ozone by Solutions of Amino Acids ( $\mu\text{mol}$  Ozone Absorbed in the KI tube)<sup>a</sup>**

Amino Acid	Ozone Introduced ( $\mu\text{mol}$ )		
	2.02	4.23	11.60
Tryptophan	0	0.15	1.15
Methionine	0.017	0.075	2.62
Tyrosine	0.074	0.294	2.54
Histidine	0.773	2.28	6.86
Cystine	0.750	2.270	6.16

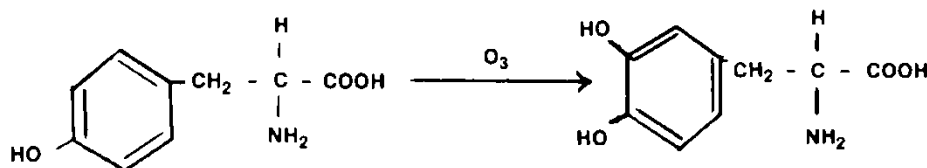
<sup>a</sup>The first tube of the series of two contained 400  $\mu\text{mol}$  of phosphate buffer (pH 7.2) and amino acids as indicated. Amino acids when added were 10  $\mu\text{mol}$ , except for cystine, which was 5  $\mu\text{mol}$ . The second tube contained 100  $\mu\text{mol}$  of potassium iodide and 400  $\mu\text{mol}$  of phosphate buffer (pH 7.2). The volume in both tubes was 5.0 ml.

### *Tryptophan Ozonation*

Tryptophan is oxidized stoichiometrically by ozone (stoichiometric ratio = 1). It appears that tryptophan oxidation is not greatly affected by pH variations (Figure 15B). Tryptophan would be slightly more easily oxidized at pH 4.6 than at pH 7.2 and 8.7. However, absorption spectra differ according to the pH values employed. There is formation of *N*-formylkynurenine, regardless of pH. However, formation of this product is at its maximum at pH 4.6. The presence of  $\text{NH}_3$  is also observed.

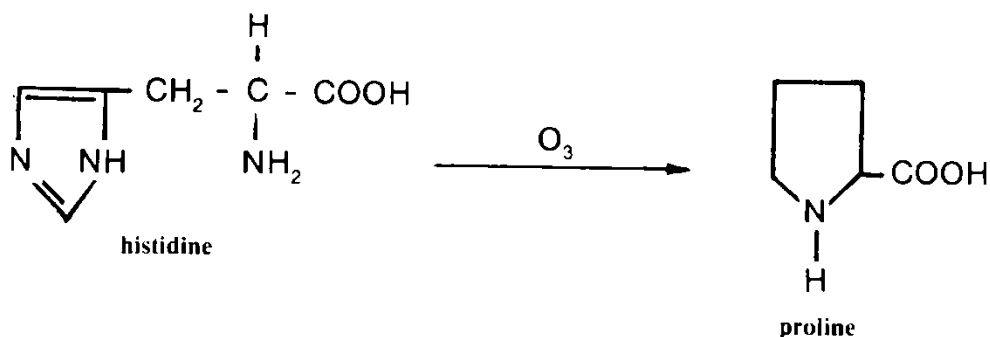
### *Tyrosine Ozonation*

Oxidizability increases with pH. A product has been identified: dihydroxyphenylalanine. Higher optical absorption is observed in the 240- to 360-nm range (Figure 15C).



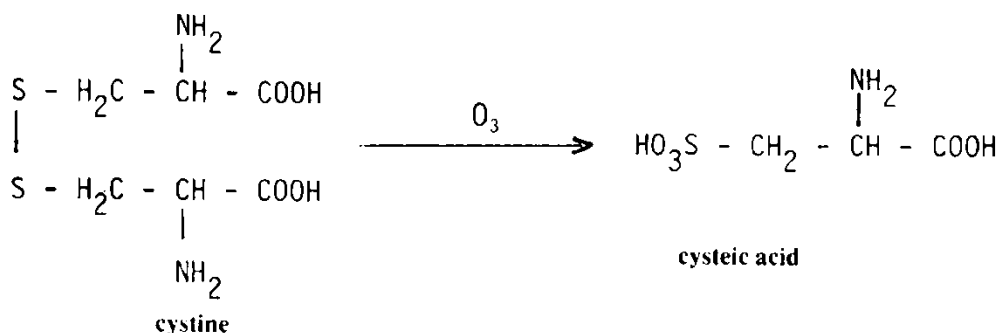
### Histidine Ozonation

Histidine degradation increases with pH (Figure 15D). Oxidation takes place with a stoichiometric ratio of less than one mole of amino acid oxidized per mole of ozone added. The main product detected is ammonia, the amount of which is equal to the amount of amino acid oxidized (at pH 7.2 and 8.7). While being metered using ninhydrin at pH 4.6, the ozonated solution develops a yellow color, probably due to the formation of proline according to:



### Cystine Ozonation

Cystine degradation increases with pH (Figure 15E). Cystine is less degraded than histidine or tyrosine. Cysteic acid has been identified as one of the main oxidation products.



Narkis et al. [13] studied ozonation of leucine with varying pH, in buffered and nonbuffered media. Oxidation was followed by measuring NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions, COD, organic nitrogen and total nitrogen. Results are shown in Figures 16,17 and Table VI. These studies show that ozonation of leucine in a nonbuffered medium depends on the initial pH. Oxidation rate increases with increasing pH and proceeds better in a buffered medium. The amount of nitrate formed in a buffered medium is two or three times as large as the amount of ammonium ions produced during the same ozonation time. According to the authors, most of the amine groups are oxidized directly to nitrates; only a portion of the amino acid