

**THE CHEMISTRY OF WATER TREATMENT PROCESSES INVOLVING
OZONE, HYDROGEN PEROXIDE AND ULTRAVIOLET RADIATION**

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Received for Review : 10 July 1987
Accepted for Publication : 5 September 1987

Abstract

Advanced oxidation processes are defined as those which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification. The theoretical and practical yield of OH from O₃ at high pH, O₃/H₂O₂, O₃/UV and H₂O₂/UV systems is reviewed. New data is presented which illustrates the importance of direct photolysis in the O₃/UV process, the effect of the H₂O₂:O₃ ratio in the O₃/H₂O₂ process, and the impact of the low extinction coefficient of H₂O₂ in the H₂O₂/UV process.

Introduction

This paper will summarize the chemistry of several water treatment processes involving combinations of ozone, hydrogen peroxide and ultraviolet radiation. The purpose is to show that these processes have much in common mechanistically, but there are significant enough differences to make one or the other more practical depending on water quality and water treatment goals.

Advanced Oxidation Processes

Ozone has been used as a chemical reagent, an industrial chemical, and an oxidant for water treatment for over eight decades (1). Ozone is known to be a powerful oxidant and disinfectant, with a thermodynamic oxidation potential that is the highest of the common oxidants. In principle, ozone should be able to oxidize inorganic substances to their highest stable oxidation states and organic compounds to carbon dioxide and water. In actual practice, however, ozone is quite selective in its oxidation reactions. In organic chemistry it is most useful for cleavage of multiple bonds and

aromatic systems, but even in these cases the rates of oxidation may be quite slow for water treatment applications. For example, ozone reacts slowly with many types of water contaminants, such as alicyclic taste and odor compounds such as geosmin and methylisoborneol (MIB) (2), aliphatic halides such as the THMs (3,4), and unactivated aromatics such as chlorinated benzenes (4). In water treatment, ozone has been most successful for enhancing the pleasant taste of water, for aiding coagulation and filtration processes, and as a first barrier to microorganisms.

There is, however, a new dimension emerging in the use of ozone in water treatment. In several laboratory and pilot scale studies, ozone is now being combined with hydrogen peroxide and ultraviolet radiation to produce results which have not been possible with ozone alone. The literature is replete with examples of O_3/UV and O_3/H_2O_2 studies in which inorganic and organic substances have been oxidized much more effectively than one can accomplish with ozone or any other common oxidant. We now understand, based on the accumulation of new information on the basic chemistry of ozone, that the success of these new processes is due to the intermediacy of the hydroxyl radical which is common to each system. We shall refer to systems such as O_3/UV and O_3/H_2O_2 as "Advanced Oxidation Processes" and include in this category other processes which generate the hydroxyl radical, namely ozone at high pH values, hydrogen peroxide with UV radiation, and ozone or hydrogen peroxide with other hydroxyl radical initiators such as metals and metal oxides.

Historical Background

Prengle and coworkers at Houston Research Inc. (HRI) were the first to see the commercial potential of the O_3/UV system. HRI showed that O_3/UV enhances the oxidation of complexed cyanides, chlorinated solvents, pesticides, and miscellaneous group parameters such as COD and BOD (5-8). Subsequently, the process also was commercialized by Westgate Research of Los Angeles (now ULTROX International) where Zeff and coworkers further extended the applications of the process (9,10). Glaze and coworkers, especially Peyton, have examined the O_3/UV process for oxidation of a number of halogenated micropollutants (3,11) and THM precursors (12) and have carried out basic studies to elucidate the mechanisms of the process (13). Several other groups have used the O_3/UV process for oxidation of a variety of organic pollutants (14-17) and the process has been taken to pilot scale for a number of types of applications (5,18,19).

The O_3/H_2O_2 system was investigated early by Nakayama et al. (20) and Hango et al. (21) for wastewater treatment, and more recently by Bollyky (22), Brunet et al. (23) and Duguet et al. (24) for drinking water treatment. Duguet et al. showed that addition of peroxide enhanced the efficiency of oxidation of several organic substances, THM precursors, and also increased the rate of ozone transfer. Studies are proceeding currently in several laboratories including our own (25), and the process is being taken to pilot plant scale by

the city of Los Angeles for removal of tri- and tetrachloroethylene in groundwater (TCE and PCE, respectively).

Hydrogen peroxide with ultraviolet radiation was studied by Berglind et al. (26) for the oxidation of humic substances, methylisoborneol, 3,4-benzopyrene (sic), chloroform and bromodichloromethane. The process is the subject of a U.S. patent (27), but little further work has been reported.

Mechanisms of Advanced Oxidation Processes

Not all of the advanced oxidation systems have been well studied and their mechanisms are not fully elucidated. It appears, however, that all involve the generation of the hydroxyl radical. The present view is that the oxidizing capability of these systems is differentiated from other common oxidants such as chlorine, chlorine dioxide, etc., because of the very high reactivity of this radical.

OZONATION AT HIGH pH VALUES

Hydroxyl radicals were postulated by Weiss (28) as intermediates in the base catalyzed decomposition of ozone. Indirect evidence for OH radicals was presented by Hoigné and Bader (29), who showed that the mechanism of ozonation seemed to change at high pH values. The relative rate constants for high pH ozonation of pairs of organic compounds were found to be the same as those for reaction of the same compounds with hydroxyl radicals generated from radiolysis of water.

Hoigné's group (30-32) and independently, Hart et al. (33-34) used advanced spectrokinetic methods to elucidate the mechanism by which ozone decomposes in water. A complex chain mechanism was revealed that involves a series of single-electron and atom transfer processes (Figure 1) and the intermediacy of OH radicals. Staehelin and Hoigné showed that a variety of substances can initiate the chain, including hydroxide, hydroperoxide, formate and ferrous ions, and even humic substances (35). Although direct spectroscopic evidence for the OH radical in aqueous ozone systems has not been found, the indirect evidence is overwhelming that OH is the key reactive intermediate when ozone decomposes in water.

In very pure water, OH reacts with ozone so that the chain propagating steps shown in the circle in Figure 1 can repeat again and again. Hundreds of ozone molecules may be decomposed by a single initiation step. The result is that ozone can have a very short half-life in distilled water at pH 7 (36). In the presence of common water contaminants, for example, bicarbonate, carbonate and the organic constituents of humic substances, the cycle can be broken by trapping of the hydroxyl radical, and of course, the chain also may be broken by radical-radical coupling processes.

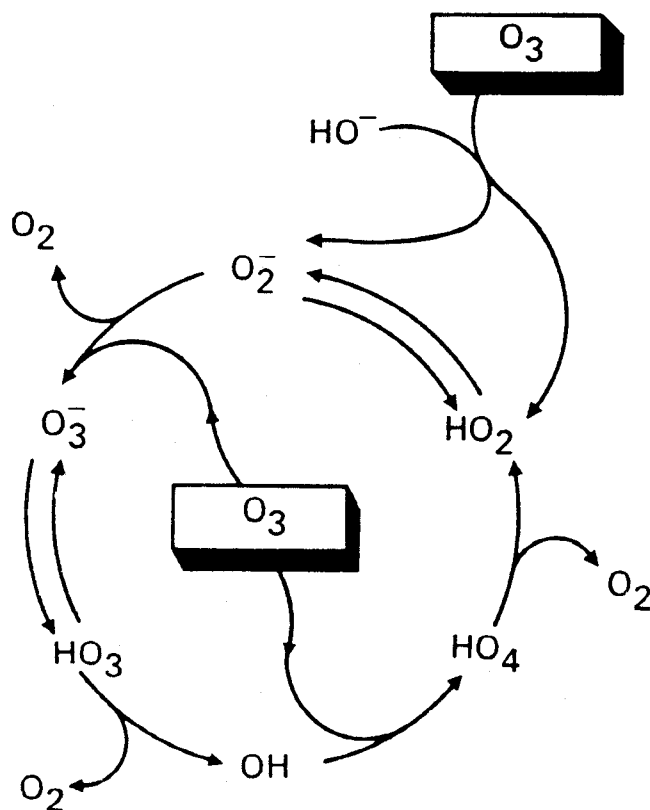


Figure 1. Scheme showing the principal species in the decomposition of ozone in pure water initiated by hydroxide ions (after Staehelin et al., reference 32).

Rate constants for reaction of OH with most substances are extremely large, indicating that the reactions are very fast; some occur almost every time an OH radical collides with a molecule of the substance. One of the major water contaminants, bicarbonate ion, will trap hydroxyl radicals with such efficiency that the half-life of ozone in distilled water at pH ~ 7 increases from about 10^3 seconds in distilled water to 10^4 seconds in 2 mM HCO_3^- (36).

If organic micropollutants are present when ozone decomposes, they too will react with hydroxyl radicals, but they must compete with all of the other OH traps present. If the concentration of the micropollutant organics is in the micromolar range or below, they may be at a distinct disadvantage compared to matrix contaminants such as

bicarbonate ions or humic materials, which may be present at concentrations several orders of magnitude higher (35).¹

As Hoigné and coworkers have observed, the mechanism of the reaction of ozone with another substance M may involve both direct reactions of M with ozone and reaction of M with OH radicals, even if the pH of the system is near neutral (35). This is because OH-promoters such as hydrogen peroxide and superoxide ion, O₂⁻, are formed in the course of direct ozonation processes. Also, there may be contaminants in the water which act as promoters. Thus, when ozone reacts with substances in natural waters it is almost surely reacting by a combination of direct O₃ and OH pathways, the relative proportions of which will depend on the various contaminants present or added. The mechanism may even become more radical in character as the reaction proceeds.²

At higher pH values there is an important factor that works against the effectiveness of ozonation processes. Hoigné has pointed out that increasing the pH will not necessarily increase the rate of OH radical destruction of a substrate because of enhanced trapping effects (29). At pH values greater than 10.3, carbonate ion is a more prevalent species than bicarbonate ion, and the rate constant for the reaction of OH with carbonate ion is over twenty times greater than with bicarbonate ion. On the other hand, ozonation is not commonly carried out at pH values above 10.3, so the role of carbonate ion may not be very severe as these considerations indicate.

Further studies are needed to carefully document the advantages and disadvantages of using high pH conditions to enhance ozonations in waters with different alkalinity values. Figure 2 shows data from a study being carried out in our laboratory where the rate constant for ozonation of trichloroethylene is measured in a CSTR treating a high alkalinity groundwater from a well in North Hollywood (alkalinity 200 mg/L as CaCO₃; pH 7.3; DOC 1.1 mg/L; Fe, Mn less than 0.1 mg/L).

¹ In the O₃/H₂O₂ oxidation of TCE in the presence of 300 mg/L (as CaCO₃) of bicarbonate ion, we calculate that only about 4% of the transferred ozone is utilized for the destruction of 90% of 600 ug/L of TCE (25).

² This may explain apparent discrepancies in the literature on such questions as the destruction of THM formation potential by ozonation, where some workers see an enhancement of THMFP by ozone and others do not (37). Under some conditions, OH radicals apparently are produced by initiators present in the water, and these radicals may hydroxylate benzenoid species to form THM precursors. Under other conditions, the radicals either are not formed in such abundance, or are quenched by other species (38).

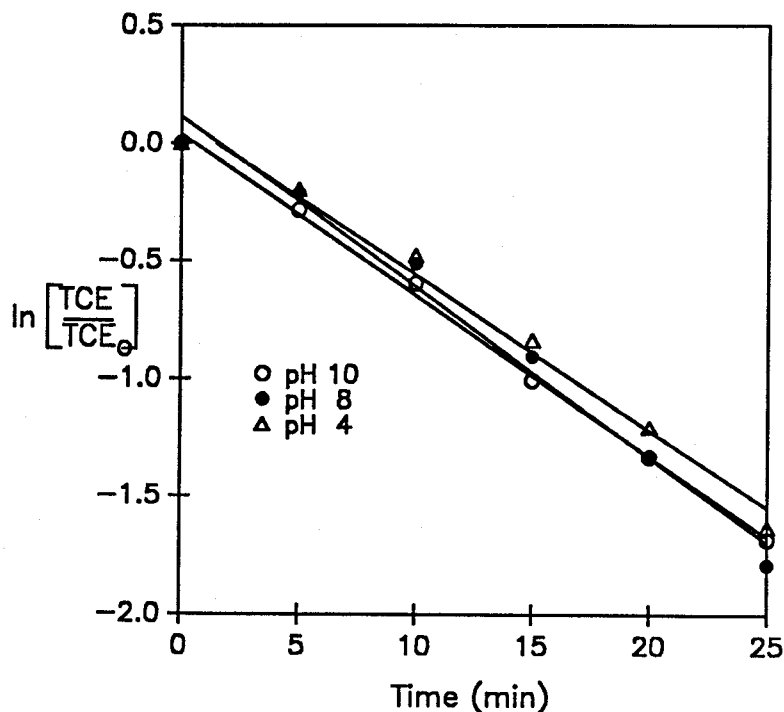
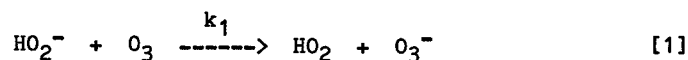


Figure 2. Effect of pH on the ozonation of trichloroethylene (TCE) in North Hollywood Well No. 26 water. Bicarbonate alkalinity: 200 mg/L; TOC 1.1 mg/L; pH adjusted upwards with sodium hydroxide, downward with hydrochloric acid; 70 liter CSTR with ozone generated from pure oxygen.

As Figure 2 shows, adjusting the pH from 4 to 10 has little effect on the destruction of TCE. We suspect that this may be due to a cancellation of the promoting effect of hydroxide ion and the scavenging effect of carbonate vs. bicarbonate ions, and therefore may not be typical behavior for a water of lower alkalinity. However, the results illustrate that rate enhancements from pH changes below 10 or 11 may be minimal.

OZONE WITH HYDROGEN PEROXIDE

Hart and coworkers (33) and Staehelin and Hoigné (30) showed that the conjugate base of H_2O_2 can initiate the ozone decomposition cycle by a single electron transfer process involving the conjugate base of hydrogen peroxide, HO_2^- :



This initiates the decomposition of ozone resulting in the formation of hydroxyl radical. Exploiting this effect, Duguet et al. (24) showed that the efficiency of color removal by ozone is accelerated by hydrogen peroxide. The dependence on the concentration of peroxide suggests that H₂O₂ is acting as a scavenger at high concentrations.

In recent studies in our laboratory we are exploring the O₃/H₂O₂ system with several substrates including chloroethenes and several taste and odor compounds. Figure 3 shows rate data for the destruction of tetrachloroethylene in a groundwater from the same area in Los Angeles from which the sample referred to earlier was taken. The alkalinity of this water is somewhat higher than the other (300 mg/L at CaCO₃), but other water quality parameters are similar.

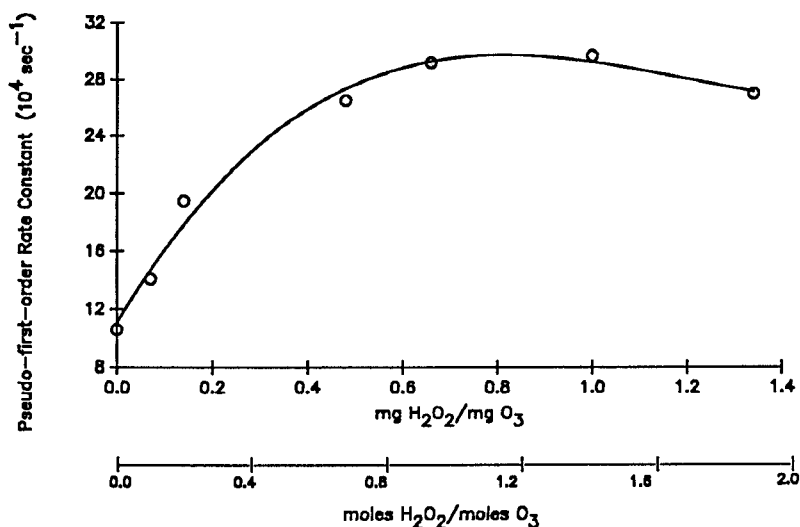
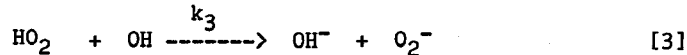
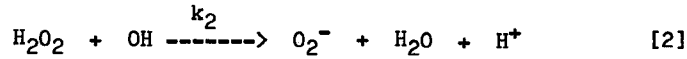


Figure 3. Effect of hydrogen peroxide on the pseudo first-order rate constants of oxidation of TCE in North Hollywood Well No. 14 water. Alkalinity: 300 mg/L; 70-L CSTR with ozone generated from pure oxygen. O₃ scale is dose rate; utilization > 90%.

In these experiments, to be reported in more detail later, the peroxide and ozone were fed simultaneously into the reactor, ozone and peroxide residuals were generally below 0.1 mg/L, and ozone utilization greater than 90%). The pseudo first-order rate constants show a hyperbolic dependence on peroxide with a maximum at a ratio of about one mole of peroxide per mole of ozone. This is the function expected if peroxide acts as a promoter as well as an OH scavenger. Indeed, it is known that peroxide will act as an OH radical trap as well as an initiator.

The rate constant for reactions [2] and [3] are $2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively (39):



It should be noted, however, that superoxide ion, O_2^- , also is formed in equations [2] and [3], and since superoxide also promotes the decomposition of ozone, it is not clear why peroxide inhibits the decomposition of TCE at high H_2O_2 levels. If one assumes that superoxide reacts primarily by some other pathway than with ozone, then one may derive equation 4:

$$-d(\ln[M]/[M_0])/dt = k_0 \quad [4]$$

where

$$k_0 = \frac{k_M k_1 K_{\text{per}} [\text{H}_2\text{O}_2] [\text{O}_3] / [\text{H}^+]}{k_M [M] + (k_2 + k_3 K_{\text{per}} / [\text{H}^+]) [\text{H}_2\text{O}_2] + \sum k_1 [S_i]}$$

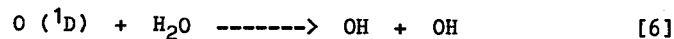
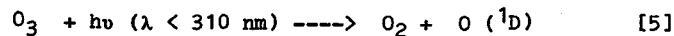
K_{per} is the dissociation constant of hydrogen peroxide (1.6×10^{-12}), k_M is the rate constant for the reaction of OH with substrate, in this case TCE or PCE, and $\sum S_i$ symbolizes other matrix components that trap OH with rate constants k_1 , the most important of which are dissolved organic carbon (humic substances), and bicarbonate or carbonate ion (36).

Alternatively, the shape of Figure 3 may be related to the fact that the reaction is being carried out in a CSTR. That is, at high peroxide doses, the rate constant is mass transfer limited.

In any case, the results of the laboratory scale tests on the oxidation of TCE and PCE are so encouraging that the city of Los Angeles currently is sponsoring pilot scale tests to evaluate the large scale potential of the $\text{O}_3/\text{H}_2\text{O}_2$ system for remediation of contaminated groundwater in the San Fernando Valley (40).

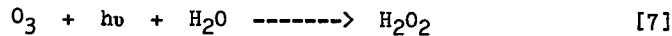
OZONE WITH ULTRAVIOLET RADIATION

The photolysis of ozone in wet air produces hydroxyl radicals by a two step process (41):



Previously it was assumed (8) that photolysis of ozone in water would proceed by a similar pathway; however Taube (42) showed, and more recently Peyton and Glaze (13,18) confirmed that this is not the

case. Rather, hydrogen peroxide is formed in a process where OH radicals, if formed at all, do not escape from the solvent cage. The overall reaction is :



Equation [7] would appear to say that the O₃/UV and O₃/H₂O₂ processes are one and the same; in the former, one is merely forming hydrogen peroxide in situ, rather than adding it from an external source. Indeed, for some substrates that is the case, as will be discussed below. For other substrates which absorb ultraviolet radiation, the O₃/UV process can be much more. This is illustrated by the O₃/UV oxidation of tetrachloroethylene, first reported by Peyton et al. (3), and more recently explored in a groundwater matrix by our group in Los Angeles.

Tetrachloroethylene (PCE) absorbs ultraviolet radiation at 254 nm only weakly, but sufficiently so that direct photolysis is a significant contributor to the overall decay of PCE when the compound is exposed to ozone and 254 nm radiation in a CSTR reactor. Figure 4 is a plot of pseudo first-order rate constants for a series of runs in which the ozone dose was varied while keeping the UV dose constant.

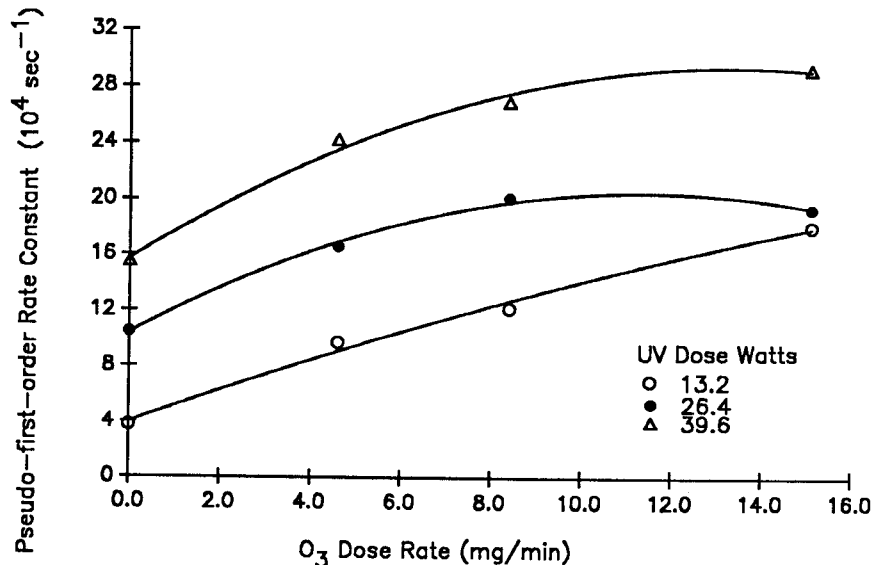


Figure 4. Effect of ozone and UV dose rates on the photolytic ozonation of perchloroethylene (PCE) in North Hollywood Well No. 14 water. Rate constants (s⁻¹) multiplied by 10⁴; UV dose in watts/L at 254 nm calibrated by chemical actinometry.

For a given UV dose, the data approximately fit a simple relationship:

$$k_o = k_p + k_{ox}D^n = k_p + k' \quad [8]$$

where k_p is the direct photolysis constant, k_{ox} is related to the constant for OH radical reaction with PCE, D is the ozone dose rate, and n is a coefficient with a value near unity (3). The value of k_p obtained from an experiment in which D was zero (only oxygen was used) is in good agreement with the extrapolated value from Figure 4.

Similar experiments were carried out with trichloroethylene (TCE) with markedly different and revealing results. Figure 5 shows that the O_3/UV oxidation of TCE is only weakly dependent on the UV flux. The extrapolated value at zero ozone dose is in good agreement with the rate constant obtained in the "UV only" experiments.

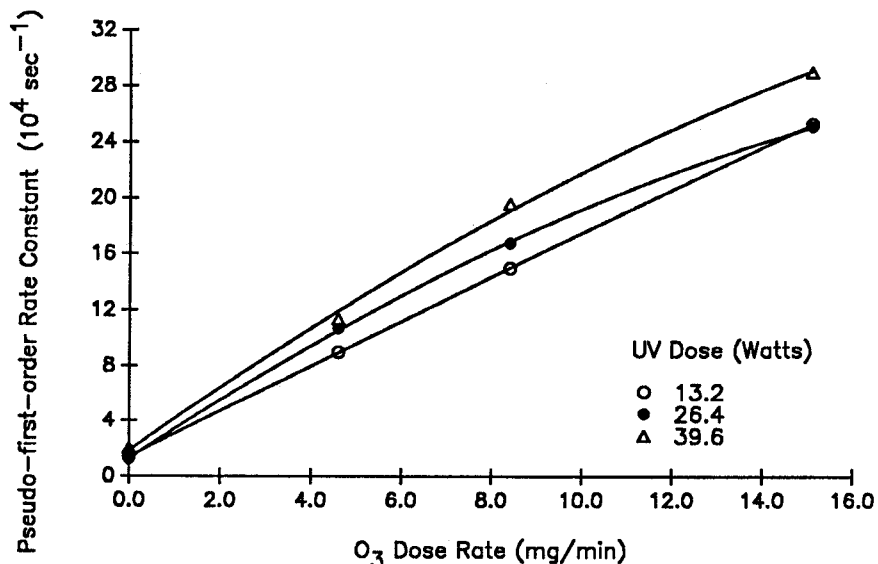
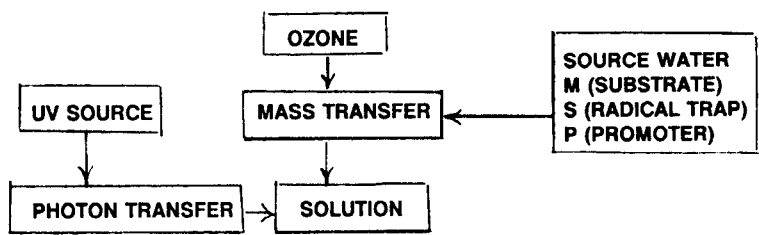


Figure 5. Effect of ozone and UV dose rates on the photolytic ozonation of trichloroethylene (TCE) in North Hollywood well water. Rate constants multiplied by 10^4 ; UV dose in watts/L at 254 nm calibrated by chemical actinometry.

The TCE and PCE data from these experiments demonstrate what Prengle and coworkers claimed years ago (8): that the O_3/UV process is, at the same time, an oxidation process and a photolysis process. Figure 6 illustrates the various elements of the process, including direct ozonation, decomposition of ozone (OH radical chemistry) and direct photolysis of M and hydrogen peroxide. The relative importance of these processes will depend on an extraordinary number of factors including: the intensity and wavelength of the UV radiation, the

ratio of O₃:UV doses, the concentration of M, promoters and radical traps, and others.

MASS TRANSFER AND PHOTON TRANSFER



CHEMICAL PROCESSES

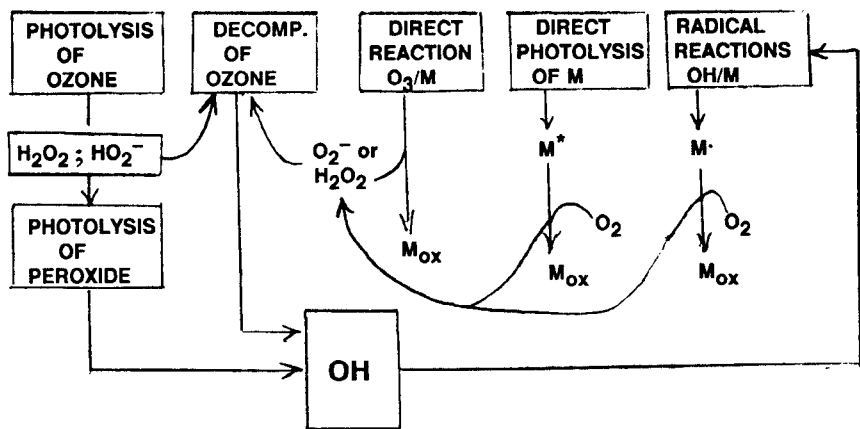


Figure 6. Schematic diagram of the elements of mass and photon transfer, and chemical processes involved in the O₃/UV process.

When a substance absorbs strongly in the UV region, large fluxes of UV radiation will accelerate the destruction of the substance. This is the case for PCE and presumably for other UV absorbing substances such as aromatic halides. For some photolytically labile substances such as some pesticides, k_p is so large that little is to be gained from using ozone.

On the other hand, when the substance of concern is not photolyzed directly with much efficiency, the use of UV radiation to generate hydrogen peroxide makes little sense.³ In such cases it is preferable to add hydrogen peroxide from an external source. Metering of peroxide into a water stream is a trivial task compared to the use of UV lamps with their attendant problems of clouding and flux decay. Our view is that both processes should be considered in a feasibility study, but except when direct photolysis is a major factor, the O_3/H_2O_2 process is heavily favored.

HYDROGEN PEROXIDE WITH ULTRAVIOLET RADIATION

In principle, the most direct method for the generation of hydroxyl radicals is through cleavage of hydrogen peroxide, a relatively inexpensive and readily available chemical intermediate. Photolysis of hydrogen peroxide is known to yield hydroxyl radicals by a direct process, i.e., with a quantum yield of two OH radicals formed per quantum of radiation absorbed (43):



Unfortunately, the molar extinction coefficient of hydrogen peroxide at 254 nm is only $19.6 M^{-1} s^{-1}$ (43), which is exceptionally low for a primary absorber in a photochemical process. By comparison, the value for ozone is $3300 M^{-1}$. This means that in order to generate a sufficient level of OH radicals, one must have a rather high concentration of hydrogen peroxide in the medium.

Figure 7 shows data from a kinetic study in which hydrogen peroxide is being metered into a CSTR at a rate of 10 mg/min while photolyzing the solution with three 13-watt low pressure mercury arc lamps (greater than 90% UV energy at 254 nm). Trichloroethylene, which was spiked into the original solution at 500 ug/L, and residual hydrogen peroxide were monitored as the reaction proceeded. Figure 7 shows that TCE is decomposed at a reasonable rate compared to the O_3/H_2O_2 data in Figure 3, but hydrogen peroxide accumulates to unacceptable levels. We conclude that the H_2O_2/UV is unlikely to be a practical process for drinking water treatment until this problem is solved; however, for wastewater treatment or other purposes it might be useful.

³ Many applications of the ozone/UV process, including some current commercial reactors, use UV intensities which are extremely high and costly. There is an optimum ratio of UV flux (in Einsteins/min):ozone dose (in moles/min) for each system, but in the absence of much direct photolysis the ratio is probably less than 0.5. In a study of the O_3/UV oxidation of THM precursors the optimum ratio was 0.3 (18).

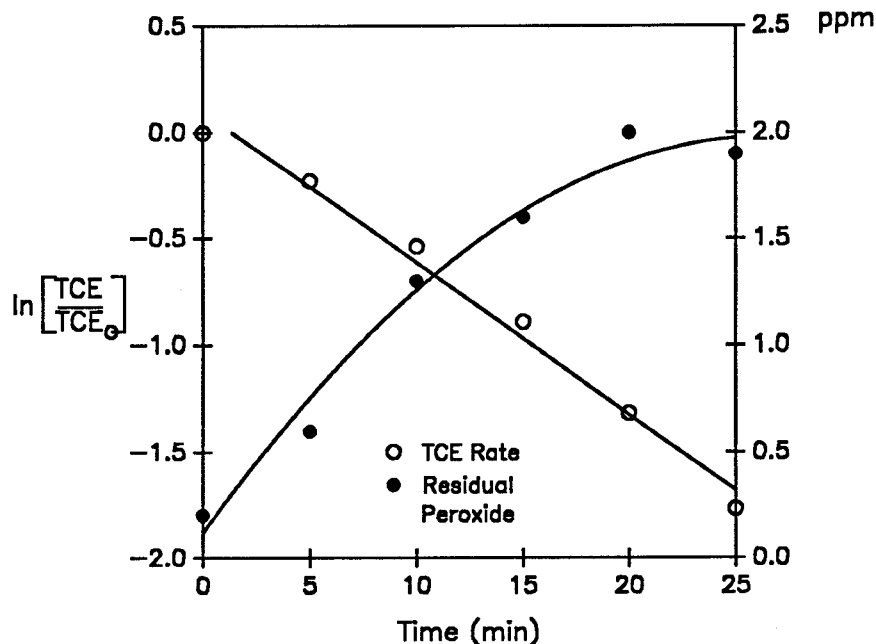


Figure 7. Pseudo first-order plot for destruction of TCE by H₂O₂/UV process in North Hollywood Well No. 14 water. Reaction carried out in 70-L CSTR with feed rate of 10 mg H₂O₂ per minute. Residual peroxide determined by horseradish peroxidase fluorimetry (44).

SUMMARY OF HYDROXYL RADICAL GENERATING PROCESSES

Table I is a summary of the chemistry involved in the generation of hydroxyl radicals from the four processes considered in this review. As noted above, the stoichiometric yield of hydroxyl radicals is greatest from the photolysis of hydrogen peroxide. As Table II shows, however, ozone photolysis yields more radicals in practice because of the higher molar extinction coefficient of ozone compared to hydrogen peroxide.

Of the four processes, the O₃/H₂O₂ process should have a high yield of OH radicals, is most amenable to adaptation in existing water treatment plant designs, and should be relatively cost-effective. The use of ozone at high pH values may be comparable in cost/effectiveness, but there is little field data on this process. The O₃/UV process will be difficult to adopt on a large scale, but may be useful for small water and wastewater treatment plants, particularly when the substrates of concern are strong UV absorbers.

TABLE I. THEORETICAL AMOUNTS OF OXIDANTS AND UV REQUIRED FOR FORMATION OF HYDROXYL RADICAL IN OZONE - PEROXIDE - UV SYSTEMS

System	Moles of Oxidant Consumed per Mole of OH Formed		
	O ₃	UV ^a	H ₂ O ₂
Ozone - Hydroxide Ion ^b	1.5	---	---
Ozone - UV	1.5	0.5	(0.5) ^c
Ozone - Hydrogen Peroxide ^b	1.0	---	0.5
Hydrogen Peroxide - UV	---	0.5	0.5

^a Moles of photons (Einsteins) required for each mole of OH formed.

^b Assumes that superoxide formed in the primary step yields one OH radical per O₂⁻, which may not be the case in certain waters.

^c Hydrogen peroxide formed *in situ* (13,42).

TABLE II. THEORETICAL FORMATION OF HYDROXYL RADICALS FROM PHOTOLYSIS OF OZONE AND HYDROGEN PEROXIDE

	Molar Absorptivity 254 (M ⁻¹ cm ⁻¹)	Stoichiometry	OH Radicals Formed ^a per Incident Photon
H ₂ O ₂	20	H ₂ O ₂ ----> 2(OH)	0.09
O ₃	3,300	3(O ₃) ----> 2(OH)	2.00

^a Assumes 10-cm path length; quantum yield as predicted from stoichiometry; [O₃] and [H₂O₂] at 1 x 10⁻⁴M.

Acknowledgement

The authors are grateful to the City of Los Angeles Department of Water and Power for support of this work, partially with funds supplied by the U.S. Environmental Protection Agency through Cooperative Agreement CR-813188, and to E. Marco Aieta, Rhodes Trussell and Carol Tate of James M. Montgomery Consulting Engineers for useful discussions. This article has not been subjected to review by the

U.S. EPA. Therefore, it does not necessarily reflect the views of this agency, and no official endorsement should be inferred.

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Key Words

Ozone, Hydrogen Peroxide, Ultraviolet Radiation, Water Treatment Processes, Chemistry, Hydroxyl Free Radicals, Ozone Decomposition Products, Trichloroethylene Oxidation, Tetrachloroethylene Oxidation, Photolysis of Organic Compounds, Advanced Oxidation Process Mechanisms, Ozone/H₂O₂, Ozone/UV

Résumé

Les procédés avancés d'oxydation sont définis comme ceux qui impliquent la génération de radicaux hydroxyles en quantité suffisante pour affecter la purification de l'eau. Les rendements théoriques et pratiques de (OH)· à partir d'ozone, à pH élevé, et des systèmes O₃/H₂O₂, O₃/UV et H₂O₂/UV sont passés en revue. De nouveaux résultats sont présentés qui illustrent l'importance de la photolyse directe dans le système O₃/UV, l'influence du rapport H₂O₂:O₃ dans le procédé O₃/H₂O₂ et l'impact du faible coefficient d'extinction de H₂O₂ dans le procédé H₂O₂/UV.

Zusammenfassung

Moderne Oxidationsverfahren sind solche, welche die Erzeugung von Hydroxylradikalen in Mengen ermöglichen, wie sie zur Wasserreinigung nötig sind. Es werden die theoretischen und tatsächlichen Ausbeuten von (OH)·, hergestellt mittels O₃ bei hohen pH-Werten, besprochen, wie auch aus Reaktionen mit O₃/H₂O₂, O₃/UV, und H₂O₂/UV. Neue Daten werden präsentiert, welche die Wichtigkeit der direkten Photolyse im O₃/UV-Prozess, die des H₂O₂:O₃-Verhältnisses im O₃/H₂O₂-Prozess und den Einfluss des niedrigen Extinktions-Koeffizienten von H₂O₂ beim H₂O₂/UV-Prozess belegen.