

OZONATION OF WATER: SELECTIVITY AND RATE OF OXIDATION OF SOLUTES

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Abstract

The reactions of ozone with dissolved organics in aqueous media are considered in terms of two reaction pathways: direct reactions of ozone and free radical reactions involving a hydroxyl free radical intermediate. The selectivity and reaction rate are correlated with the molecular structure of the organic compound. The effect of free radical quenchers are examined.

At the 2nd IOI Symposium (Montreal 1975) we reported on the two main sequences of reactions by which ozone initiates oxidations of solutes in water: (i) the direct reactions of ozone and (ii) the reactions which follow a preliminary decomposition of ozone to OH^\cdot radicals (Fig. 1). These two pathways of reactions lead to different selectivities with which different types of solutes are oxidized, and they also lead to different types of product formations. The yields of these two sequences of reactions are furthermore regulated by some other process parameters (1,2). In order to make further progress in ozonation treatment, a more systematic insight into the rates of these main chemical reactions is needed. We think that it is urgent that experimental methods are developed which allow one to distinguish between these two pathways of reactions as well as that ozone chemists have access to lists of chemical rate data on the reactions involved.

Figure 1 recapitulates the situation. During ozonation, part of the ozone added reacts directly with the solutes, and a part of it decomposes to radicals before it reacts with solutes or before it is stripped off. The higher the pH, the faster goes this decomposition: it is initiated by hydroxyl ions (OH^-). It is additionally accelerated by a chain reaction for which the radicals formed act as chain carriers. Because of this chain reaction, the lifetime of ozone in water depends also on solutes yielding radical-type intermediates which additionally catalyse the decomposition of ozone and on solutes which scavenge the OH^\cdot radicals (3). Such scavengers quench the chain reaction and stabilize somewhat the ozone (examples: bicarbonate ions, aliphatic alcohols). In water from Lake Zurich or Lake Constance or from the Rhine at Dusseldorf (all approximately pH 8.0), half of the ozone decays within about 10 minutes. By this reaction, about 25 mole% of the ozone added is converted into OH^\cdot (3). At elevated pH values, the OH^\cdot reactions become dominant.

Kinetic constants as well as product formations resulting from reactions of OH^\cdot radicals with solutes (R-Type reactions) are well known from other disciplines such as from radiation chemistry and from projects which were performed to get clearance for food

treated by high energy irradiation or from projects aimed at learning more about the chemistry taking place in medical high-energy radiation therapy. Last year we showed (3) how to apply known rate data on OH radical reactions for quantifying the effect of these radicals on the oxidation of solutes in water. Now, in chapter 3, we will compare the numerical values to estimate their contribution to the oxidations.

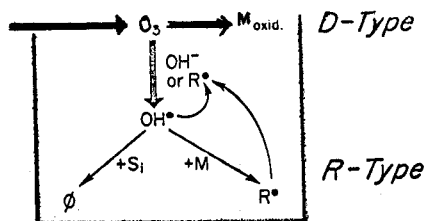


FIG. I

Scheme of reactions

For some solutes present in a water, the direct reactions of molecular ozone with solutes (D-Type reactions) can also become important. Only a few rate constants for these direct reactions, however, are to be found in the literature, and those have been determined in non-aqueous solutions such as chloroform. We therefore decided to measure this type of rate constant in water and to extend the list of data by including organic compounds such as organic acids and bases. We were mainly interested in:

- 1) to see which chemical bonds react efficiently fast with ozone so as to have a fast chemical step in comparison to the overall rate of ozonation processes;
- 2) to determine rate constants of solutes for which the chemical reactions determine the rate of the overall process (substances of k values in the range of 1 to 1000 lit/mole·sec);
- 3) to learn which types of compounds react too slowly and will not be oxidized directly by ozone even during an extended ozonation.

We tried to select substances which could be useful as reference standards when testing further systems. The results with respect to the possibility of estimating selectivities for solute elimination are discussed below.

Contribution of the direct ozone reactions (D-Type reactions)

Experiments show that the rates of the direct reaction of molecular ozone with solutes M are 1st order with respect to ozone and as a rule, nearly 1st order with respect to solute concentration $[M]$: Halflifetimes of ozone (or τ_{O_3} values) have been found to be constant over a depletion range of 1:30 and for all ozone doses applied (4).

Therefore:

$$\frac{-d[M]}{dt} = -\eta \frac{dO_3}{dt} = k_{O_3} \cdot [O_3]^{1.0} \cdot [M]^{1.0} \quad (1)$$

Integration of this equation gives for the solute oxidation by this D-Reaction:

$$-\ln \frac{[M]_f}{[M]_0} = \eta \cdot k_{O_3} \overline{[O_3]} \cdot \Delta t \quad (2)$$

thereby: η = yield of solute elimination based on ozone

used per M eliminated
 $[M]_f/[M]_o$ = final solute concentration M_f at end of Δt relative to initial concentration M_o
 $[O_3]$ = mean ozone concentration during reaction period Δt
 k_{O_3} = rate constant such as defined in eq. (1)

The contribution of this D-Reaction depends only on the mean concentration of ozone $[O_3]$, the time the ozonation lasts (Δt), and the rate constant k_{O_3} .

For the relative elimination of two solutes (M_1, M_2) exposed in the same system to ozone, we may deduce from eq. 2

$$\frac{\ln ([M_1]_f / [M_1]_o)}{\ln ([M_2]_f / [M_2]_o)} = k_2 / k_1 \quad (3)$$

This shows that it is the logarithms of the ratios of final/initial concentration which is proportional to the relative rate constants with which the two solutes react.

A list of rate constants which we measured for reactions in water is given in figures 2a and 2 b.

The data have been measured by following the ozone depletion vs. time (eq. 1) or by determining the relative solute eliminations (eq. 3). The contribution of the R-Type Reaction was quenched by applying low pH values and (or) adding radical scavengers such as HCO_3^- (compare Appendix).

For easier presentation of these data we calculated the reaction time an ozonation would have to proceed (τ) in order to reduce a solute to 37% (1/e) of its initial concentration if only this D-Type Reaction were considered:

$$\tau = 1/n \cdot [O_3] \cdot k_{O_3}$$

To give numerical values which apply to a typical case, the τ_A values are calculated for the example of an ozone concentration of $[O_3]_A = 10^{-4}$ mol/l (5 g Ozone/m³) maintained over the entire ozonation process. This concentration is higher than that generally applied in water works. τ would become 10 times longer if the system was operated in such a manner so that the delivery of the ozone concentration were ten times lower. The stoichiometric factor in eq. 1 and 2, η , assumes a value of 1.0 for solutes with a free olefinic double bond, 2-3 for benzene derivatives and for many types of aliphatic compounds studied, and more than 4 for NH_3 (4). In order to make the scale of k values directly comparable to the scale of the τ_A values, we included the factor η directly in the τ scale (The resulting scale of $\tau_A \cdot \eta$ is in principle the scale of ozone depletion).

From the entries in these figures, we calculated how long an ozonation has to last in order to yield a solute elimination down to 37%. The enormous spread of the τ_A values resulting for different types of solutes shows how selectively ozone behaves. In a practical process only those compounds can be eliminated which react with τ values of less than 1,000 seconds (in our example this means $k > 10$ l/mole \cdot sec). This region is marked with a black-filled scale ordinate. The entries show that chemical bonds of the types often present in living cells or in compounds having taste, odor, or color may show appreciable reaction rates. On the other hand, compounds which do not contain reactive bonds are not attacked within an ozonation process by these molecular ozone reactions.

As this list is the first to be published, we will discuss

some characteristics of selected groups of compounds.

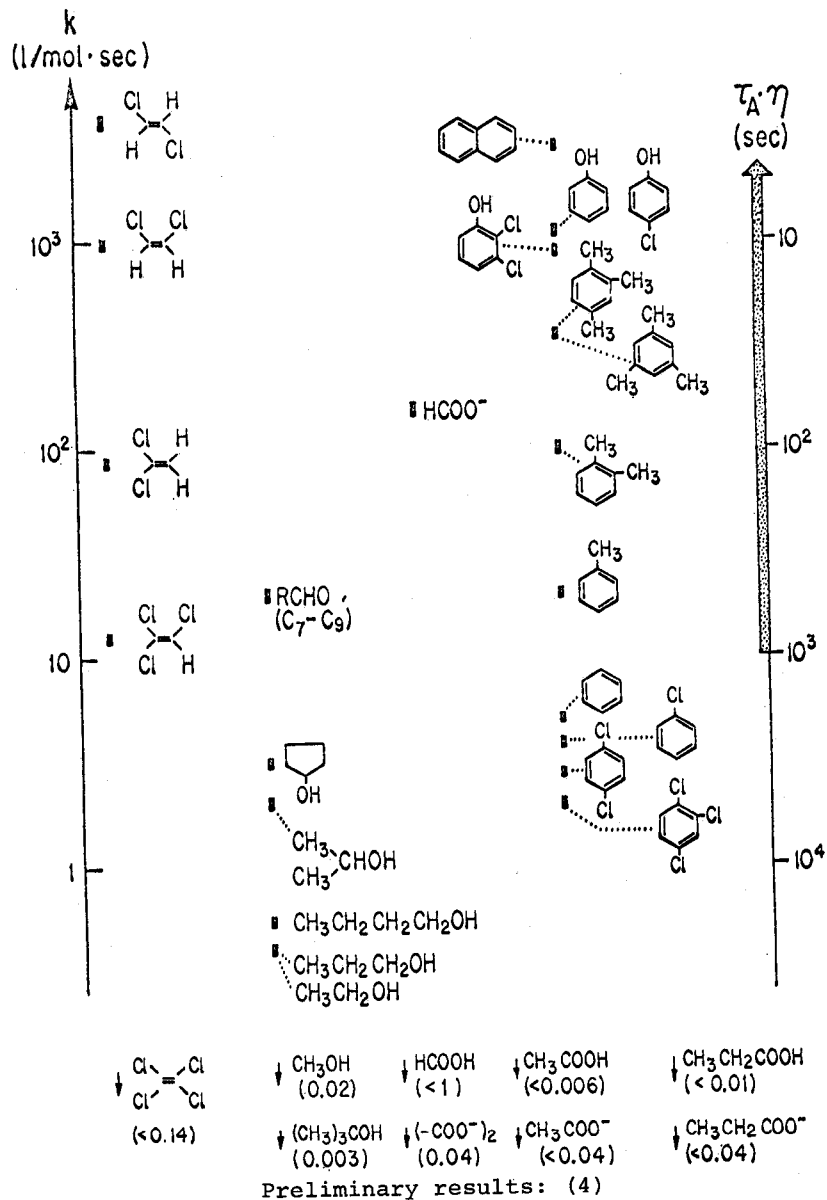
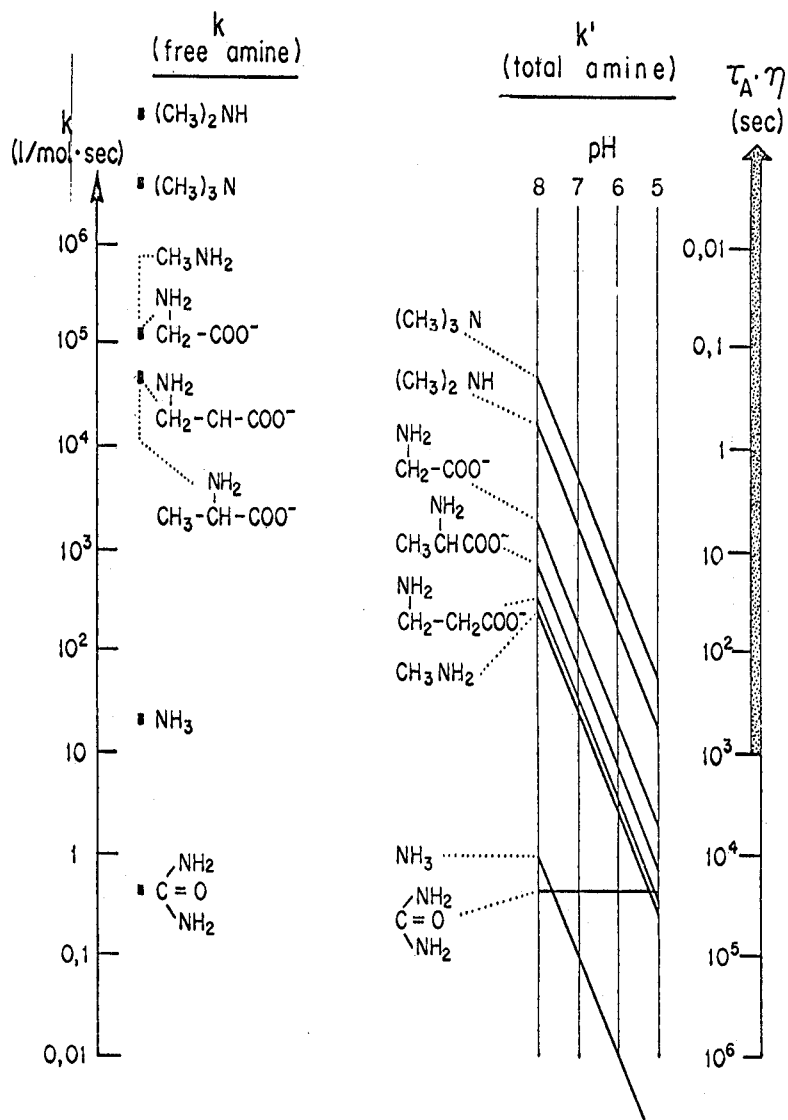


FIG. IIA

Direct ozone reactions with various C/H/O/Cl compounds

- k : 2nd order reaction rate constants for O_3 and $M_3 \rightarrow$
 τ_A : $1/(k_{O_3} \cdot [O_3])$ for $[O_3] = 10^{-4}$ mol/l ~ 5 gm/m³
 $\tau_A \cdot n$: reaction time necessary to eliminate the solute M to 37% of its initial concentration. ($n = 1-3$).



Preliminary results: (4)

FIG. IIB

Direct ozone reactions with various amino compounds

- k : 2nd order reaction rate constants for $O_3 + M \rightarrow$
- τ_A : $1/(k_{O_3} \cdot [O_3])$ for $[O_3] = 10^{-4}$ mol/l ~ 5 gm/m³
- $\tau_A \cdot n$: reaction time necessary to eliminate the solute M to 37% of its initial concentration.

Examples

Chloroethylenes: The rate constants measured correspond to those known for reactions in chloroform (5). The chlorine substitution of the double bond decreases its reactivity appreciably.

Tetrachloroethylene ("Perchlor") reacts so slowly that it cannot be oxidized by a direct ozone reaction within a day. Trichloroethylene will react only during extended ozonation treatment. In contrast, dichloroethylenes react quite fast. Free C = C double bonds would react with $k = 10^5$ l/mole · sec., that means within less than a second.

Substituted benzenes: The reaction rate of benzene is rather low. It needs hours for its oxidation even at elevated ozone concentrations. However, the rate increases if benzene is substituted by substituents which elevate the electron density in the ring. As few as three methyl groups suffice to increase the reaction rate to such a value that the reaction becomes perceptible within 10 min. Phenols and chlorophenols can be oxidized within minutes. It is interesting to note that the reaction rate constants for these compounds are about 1,000 times higher than those measured in chloroform (7,8).

Aliphatic alcohols, aldehydes, and acids: Most of these compounds react so slowly that the reaction rates are of little interest at this process oriented meeting. However, some points should be emphasized: The aliphatic group seems to have a very low reaction rate. Some activation may occur by aldehydic groups. The carbonic acids also react slowly: mainly oxalic acid which would accumulate as a daughter product of ozonation does not react within a practical time period. However, formic acid, at least in its ionic form, as formate ion, can be oxidized appreciably within minutes.

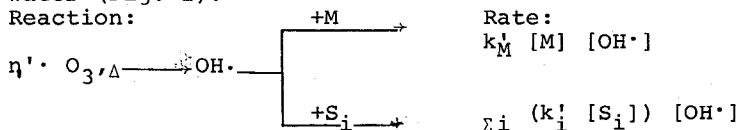
NH₃, amines, amino acids, and urea: Amines show an appreciable reaction rate when in the non-protonated form. The methylamines react about 10³ times faster than NH₃. This is due to the inactivation of the amino group by a negative charge in the case of the amino acids. As only the free amino groups show a high reactivity, the reactivity of the amino compounds corresponds to only a fraction of the rate constant of the free compound. The fraction is given by the factor

$$\alpha = \frac{\text{free amine}}{\text{total amine compound}} = \frac{R-NH_2}{R-NH_2 + R-NH_3^+}$$

α depends on the difference between the pH of the aqueous solution and the pK of the amine. In the pH region pH less than 9.0, the rate is reduced by a factor of ten when the pH is lowered by one pH unit. The corresponding overall rate constants are presented in figure 2B for pH 5 to 8.

Contribution of the OH· radical reactions (R-Type reactions)

OH· radicals formed upon ozone decomposition may oxidize a solute M or they may become consumed by scavengers present in the water (Fig. 1).



thereby:

- $O_{3,\Delta}$: O₃ decomposed during ozonation process
 η' : yield for OH· formation from O₃
[M] : concentration of solute M

$\Sigma(k'_i [S_i])$: rate of OH \cdot scavenging by all solutes present including O $_3$. [S $_i$] is the concentration and k $_i$ the reaction rate constant of the ith component
 k' : reaction rate constant with which OH \cdot reacts with M or with a scavenger solute S $_i$.

The rate of a solute oxidation (initiating step) in the presence of competing scavengers becomes:

$$-\frac{d[M]}{dt} = \eta' \cdot \frac{dO_{3,\Delta}}{dt} \cdot \frac{k'_M [M]}{k'_M [M] + (k'_i \Sigma[S_i])} \quad (4)$$

Rearrangement of this expression yields:

$$\frac{d(O_{3,\Delta}) / dt}{d[M] / dt} = \frac{1}{\eta'} (1 + \Sigma(k'_i [S_i]) / k'_M [M]) \quad (5)$$

The above shows that the specific amount of O $_3$, which must be decomposed in order to obtain a certain amount of solute elimination increases linearly with the ratio of the rate of scavenging ($\Sigma(k'_i [S_i])$) to the rate with which the solute is oxidized ($k'_M [M]$). In other words, the required amount of O $_3$ decomposition increases with the relative concentration of the scavenger concentration and the relative reaction rate constant of scavenger/solute.

In natural water, carbonate and bicarbonate ions and particularly "humic acids" may act as such scavengers. In filtered water from Lake Zurich, Lake Constance, or from the Rhine (Dusseldorf), we found for the parameter $\Sigma([S_i] \cdot k'_i)$ a value of $3 \cdot 10^4 \text{ sec}^{-1}$. An example of the inhibiting effect of the bicarbonate and carbonate on the elimination of benzene is given in Fig. 4A. The total amount of ozone, yielding a certain amount of benzene elimination, has been measured as ozone, Δ / Δ benzene (mole/mole). The result is plotted vs. the relative concentration of carbonate or bicarbonate ions. In Fig. 4B, the same specific ozone effect is plotted vs. pH for a constant sum of all carbonate species (CO $_3^{2-}$ reacts about 12 times faster with OH \cdot than HCO $_3^-$, and therefore, it has a larger inhibiting effect (3)).

We are also interested in obtaining information on the relative yield with which different solutes present in the same water (same scavenger efficiency) are eliminated by this R-Type Reaction. Eq. 4 gives an integration for the case of $\Sigma(k'_i [S_i])$ staying unchanged during the reaction (This assumption can be made for many systems we study, as the daughter products too act as scavengers) and for the case of

$$\text{rel. small } k'_M \cdot [M]: \quad \lg \frac{[M]_f}{[M]_o} = \eta' \cdot O_{3,\Delta} \cdot \frac{k'_M}{\Sigma(k'_i [S_i])} \quad (6)$$

The relative yield with which different solutes simultaneously present in the same water are eliminated by the radical reactions can be calculated from eq. 6 if the relative rate constants of the OH \cdot are known:

$$\frac{\lg [M_1]_f / [M_1]_o}{\lg [M_2]_f / [M_2]_o} = k'_2 / k'_1 \quad (7)$$

This is formally the same expression as eq. 3 which describes the selectivity of the D-Type Reaction. Fig. 3 gives a few selected values of the absolute rate constants from which the relative relations are apparent. Indicated on the right ordinate: the relative amount of O $_3$ which has to be decomposed in a water in order to reduce different solute concentrations e.g. to 37% (1/e) of their initial value when present in a same water (same

$\Sigma (k_i^1 [S_i])$ parameter). This relative value may also be expressed as a relative ozonation time necessary to reduce these compounds to the 1/e value in case of O_3 decaying at the same rate during the whole process.

Figure 3 shows that many compounds are eliminated within the same ozonation time, within the same order of magnitude of dosage of decomposed ozone. That means relatively low selectivity. Interesting exceptions are compounds such as oxalic acid and acetic acid which have, in contrast to formate ions, to be considered as highly persistent daughter products in an ozonation process (compare also the D-Type Reactions).

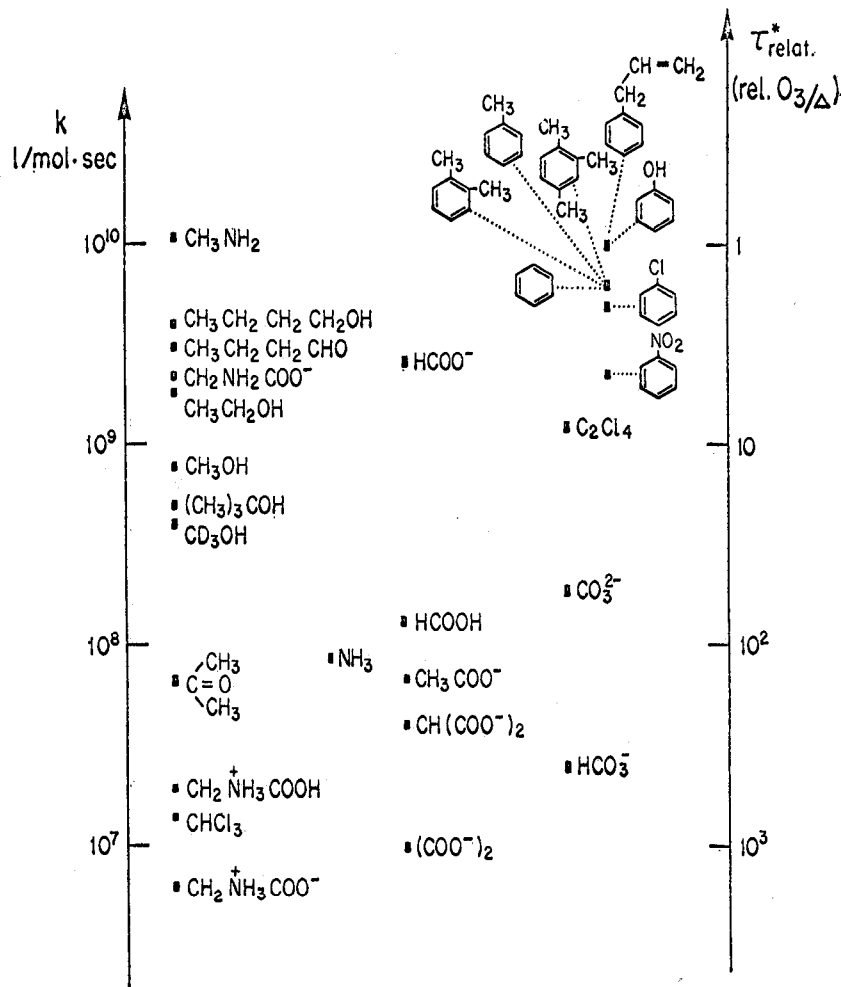


FIG. III

OH^{\bullet} radical reactions with various compounds

- k : 2nd order reaction rate constants for $OH^{\bullet} + M \rightarrow$ (selection of solutes on slowly reacting compounds). Values from literature cited in (2).
- $\tau^*_{rel.}$ or rel. ozone, : is the relative time an ozonation has to last (or the relative amount of ozone to become decom-

posed to OH[•]) in order to yield a certain ratio of solute eliminations when the solute is present as trace impurity together with OH[•] consuming solutes.

The rate of the sum of these R-Reactions is given by the rate at which ozone is decomposed in water. This rate depends on the concentration of ozone present in the water, the pH, and the concentration of carbonate or other solutes. This rate can be accelerated, as far as the ozone addition occurs, by raising the pH. For carbonate containing systems, however, it has to be kept in mind that above pH9, HCO₃⁻ dissociates significantly and forms CO₃²⁻. This has a higher scavenging efficiency which leads to a much higher inhibition (Figs. 4A and 4B).

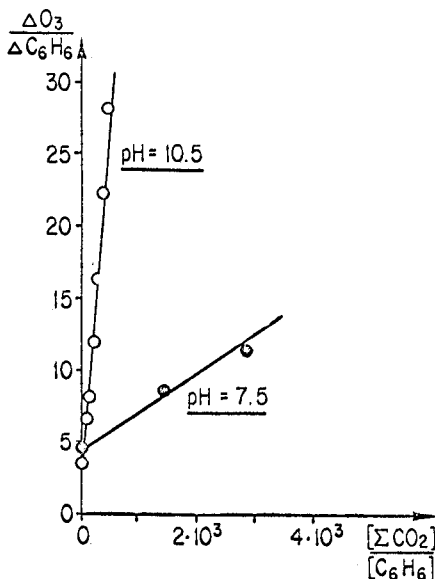


FIG. IVA

Inhibition of R-Type Reactions by radical scavengers.

Required amount of ozone consumed (ΔO_3) / benzene eliminated (Δ benzene) (mole/mole) vs. carbonate or bicarbonate concentration.

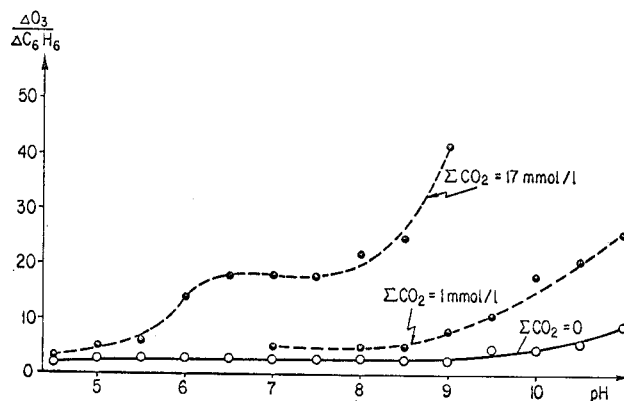


FIG. IVB

CO₂ Σ = CO₂ + H₂CO₃ + HCO₃⁻ + CO₃²⁻
 Benzene \circ conc. : Fig. A \circ 6 $\mu\text{mol/lit}$; \circ 3 $\mu\text{mol/lit}$
 Fig. B 3 $\mu\text{mol/lit}$ Values from (3)

Conclusions

Ozone is a very selective oxidant. In ozonation processes, the only solutes to be oxidized directly by O_3 are those which contain a chemical bond of special reactivity toward ozone. In most ozonation processes, part of the ozone decays during the process and forms highly reactive short-living OH radicals as intermediates. Oxidations resulting from these species have to be taken into consideration whenever persistent solutes have to be oxidized and whenever the lifetime of molecular ozone is shortened by reactions catalyzed at high pH values. Even though the OH are so reactive so as to disappear within microseconds, by many types of reactions, they still may contribute much more to the oxidations of solutes than the ozone itself. In drinking water, most of the inert types of compounds, such as those known as trace impurities, react only by this radical mechanism. This is even the case for as high concentrations of bicarbonate ions relative to the organic trace impurities as found e.g. in the water of Lake Zurich. At the Ozone Congress in Berlin (1977), we showed how this background can be used to explain quantitatively the elimination rates of trace impurities in drinking water (9).

The relative rate constants with which two different solutes are eliminated are reflected by the ratio of the logarithmic expression of final conc./initial conc. of solute 1 to solute 2:

$$\frac{\lg \frac{[M_1]_o}{[M_2]_o}}{\lg \frac{[M_1]_f}{[M_2]_f}} = k_2 / k_1 = k_{rel.}$$

This expression is formally the same for both, the Direct O_3 reaction (eq.3) and the Radical-Type Reaction (eq. 7). The $k_{rel.}$ value for the first case can be calculated from the ozone reaction rate data (Figs. 2A and 2B) and for the second case from the OH \cdot rate constants (Fig. 3). This expression shows that for both types of reactions, the logarithmic relative solute concentration has to be considered when characterizing reaction selectivities. (For the R-Reactions, we made the assumption that the scavenging reactions are overwhelming).

If product formations by ozonation are discussed, it must be kept in mind that the two different pathways of reactions lead to different daughter and daughter of daughter products and consequently to different final impurities. Each pathway constitutes a separate branched tree of alternative product formations. There are (at least) two trees of reactions which will overlap with some of their branches: one is the tree of O_3 -oxidation products, the other is the tree of OH \cdot reaction products. It appears that most experiments in the hygienic domain have been performed under laboratory conditions favoring the O_3 tree. Organic chemists who work with non-aqueous solutions leaned a ladder to this tree. The branches are full of so many interesting, unanswered questions. This is the reason why so many ozone scientists climb around in this tree. In the discussion on the elimination of inert types of impurities, however, the branched tree of OH \cdot reactions becomes larger and more important. Even to this "OH \cdot tree" a ladder is going up: the ladder built by radiation chemists during the last decades. From a classical ozone chemist's standpoint, it might have been hidden by the " O_3 tree."

Nonetheless, many molecular ozone reactions are of importance for ozonation processes mainly because of their bactericidal effects and their color and taste removal abilities. We therefore will continue to broaden our list of rate data and would like to pool it with other lists established in other laboratories.

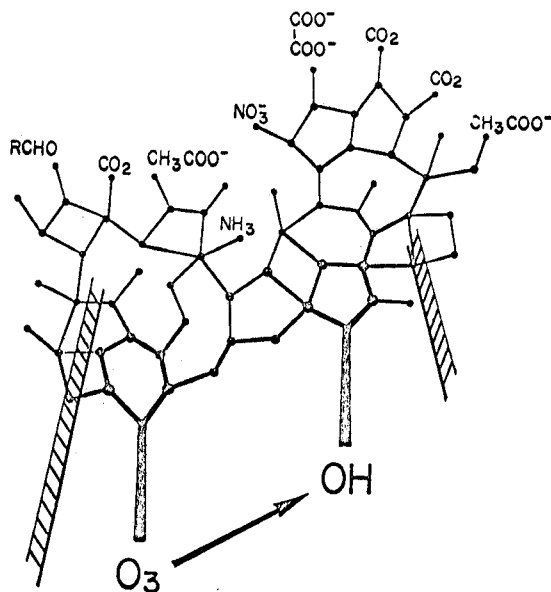


FIG. V

Branched ozone tree

AppendixMethods for the determination of rate constants of Ozone

The reactions of molecular ozone with solutes can only be determined in systems in which ozone reacts relatively fast with the solute (M) as compared with the rate with which it decomposes or with which it is stripped off (Fig. 1). In our experiments, the ozone could generally be stabilized by lowering the pH and/or by adding radical scavengers such as bicarbonate or aliphatic alcohols. The stripping off of ozone, in our case, was excluded as the work was performed in closed reactors to which a solution of a specified ozone concentration was added (2). We measured the rate of the reaction of ozone + M according to two methods:

a) Determination of absolute rate constants

The concentration of ozone was followed versus time in solutions of different solute concentrations. The rate curves were determined by following the UV absorption of ozone (258 nm) during reaction in the UV cell or by withdrawing samples from a larger reaction volume and measuring the remaining ozone by its capacity to bleach indigo solutions. Generally, the ratio of solute to ozone was at least 10 mole/mole which allowed us to keep the reactions pseudo-first order. The solute concentrations were generally set to give half life of the ozone in the range of 6 to 1,000 sec. Generally, rate constants were calculated from 5 to 10 rate curves measured for solute concentrations varying within a range of at least a factor of 10. The reaction time (ozone depletion to 1/e) was plotted versus the solute concentration in log-log plots.

From eq 1 follows:

$$\log \tau = -k + n \log [M] \quad (n = 1.0)$$

Certain stoichiometric factors were determined from oxidation

yields, $\Delta M/\Delta O_3$ in systems to which enough ozone was added to give about 30-40 % of solute elimination. Organic solutes were determined by gas liquid chromatography and NH_3 (or the resulting NO_3^-) determinations according to the methods described in (4). For solutes which do not dissociate, the pH values selected for the reactions (0.05 mol/l phosphate buffers) lay between 2 and 6. All critical solutes known to support the chain in the reaction mentioned in Fig.1 were repeatedly measured at different pH values. This allowed us to verify that the rate determinations were not made beyond the low pH region necessary for sufficient ozone stabilization. Methylamines, amino acids, and NH_3 were measured in the pH region 3 to 8, and the amount of the free amine was calculated from pK values and pH. Carbonic acids were measured between pH 2 and 5 which allowed us to separate the reactivity of the ionized species from that of the non-dissociated acid.

b) Determination of relative rate constants

Relative rate constants were determined by the competition method: In solutions containing up to 6 different solutes, the relative (logarithmic) elimination was measured upon reaction of the entire ozone added. The pH applied was generally pH2 and systems were chosen in which no significant ozone decomposition was observed in other measurements. Interferences of radical reactions were additionally excluded by comparing them with results found on samples to which an excess of a radical scavenger had been added. In each set of experiments, the relative initial solute concentrations were varied, e.g. from 1:3 to 3:1. The ozone additions were made to give 20-80% of solute consumption. The concentration measurements were made by gas liquid chromatography such as described (1). Solutes of low solubility were applied in concentrations of less than 1 mg/l. For the determination of these concentrations, the aqueous phase was extracted with pentane (2%) after all the ozone had reacted, and gas chromatography was carried out on this extract.

The determination of rate constants by the two different methods produced corresponding results. These also agreed with the determined eliminations of trace impurities in filtered lake water (10).

References

1. J. HOIGNE AND H. BADER, Proc. of the Second International Symposium on Ozone Technology, International Ozone Institute, Cleveland, Ohio (1976).
2. J. HOIGNE AND H. BADER, Water Research 10, 377-386 (1976).
3. J. HOIGNE AND H. BADER, Tagung Fachgruppe Wasserchemie DChG, Kiel 1976, Vom Wasser 48, 283-304 (1977).
4. J. HOIGNE AND H. BADER, Environm. Sci. and Technol., in preparation.
5. D.G. WILLIAMSON AND R.J. CVETANOVIC, J. Am. Chem. Soc. 90, 3668-3672 (1968).
6. D.G. WILLIAMSON AND R.J. CVETANOVIC, J. Am. Chem. Soc. 90, 4248-4252.
7. J.P. WIBAUT AND F.L.J. SIXMA, Recueil trav. chim. 71, 761-770 (1952).
8. T.W. NAKAGAWA, L.J. ANDREWS, AND R.M. KEEFER, J. Am. Chem. Soc., 82, 269-276 (1960).
9. J. HOIGNE AND H. BADER, Wasser Berlin '77, Collogium Verlag, pp. 26]-276, Otto H. Hess, Berlin, AMK Berlin (1978).
10. F. ZURCHER, H. BADER, AND J. HOIGNE, manuscript in preparation.

Key Words

Direct ozone reactions, free radical intermediate reactions

Auszug

Die Reaktion des Ozons mit in wässriger Umgebung gelösten organischen Stoffen wird auf zweierlei Weisen berücksichtigt; die direkte Reaktion des Ozons und die freie radikalische Reaktion, die einen hydroxylfreiradikalischen Zwischenstadium beinhaltet. Das Verhältnis der Selektivität und der Reaktion hängen von den molekularen Bestandteilen des organischen Stoffes ab. Die Wirkung der freiradikalischen Löschung wird geprüft.

Abrégé

Deux routes possibles des réactions de l'ozone avec des composés organiques en milieu aqueux sont discutées; les réactions directes de l'ozone et celles des radicaux libres avec la participation d'un radical libre intermédiaire d'hydroxyle. La sélectivité et la rapidité de la réaction sont reliés à la structure moléculaire des composés organiques. L'effet d'agents désactivants des radicaux libres est examiné.