Kinetics of Ozone Decomposition and Reaction with Organics in Water

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The decomposition of ozone in water is found to be second order at pH 2 and 4 with the rate insensitive to pH. At pH 6 the reaction order is 3/2 to 2 and at pH 8 it is first order. Above pH 6 the rate increases rapidly with pH. Ozonation can greatly reduce the organic matter in waste water. The reaction rate of ozone with organics in flocculated secondary sewage effluent is found to depend on the rate of ozone decomposition, which is independent of the subsequent reaction with the organics.

It has been recognized for some time that ozonation of water supplies provides a sterilized product of superior taste and odor. Recent studies (*1* to *5*) have also indicated that the BOD and total organic content can be reduced by ozone. This offers the possibility of producing potable water from waste water at a cost considerably less than that of desalination. Furthermore, every city and plant has waste water, and if proper treatment can be found, waste waters could be recycled, alleviating both water supply and waste disposal problems.

Since ozone may decompose rapidly in water solutions, a better understanding of the variables affecting the decomposition of ozone and its reaction with organic matter in waste water is needed. A number of rather thorough studies have been made of ozone decomposition (*6* to *12*), but their chief characteristic is their disagreement. For this reason we have made a fairly extensive study of ozone decomposition rates in water at a variety of temperatures and pH's. This is followed by some initial work on the reaction of ozone with organics in water.

DECOMPOSITION OF OZONE IN WATER

Table 1 shows the range of variables covered by various investigators and their conclusions concerning the reaction order relative to ozone. The results of Stumm (*11*) at pH 8 and above and of Rothmund and Burgstaller (*9*) at pH 2 to 4 agree with those of the present investigators. All the others are in apparent disagreement.

The results of Alder and Hill (*6*) are interesting in that they measured the decomposition rate by iodometric and spectrophotometric methods and obtained very different results. They postulated that the iodometric method gave the total reducibles and proposed the following mechanism for O_3 decomposition:

$$O_3 + H_2O \xrightarrow{k_1} HO_3^+ + OH^- \tag{1}$$

$$HO_3^+ + OH^- \underset{k_2'}{\overset{k_2}{\rightleftarrows}} 2HO_2 \tag{2}$$

$$O_3 + HO_2 \xrightarrow{k_3} HO + 2O_2 \tag{3}$$

$$HO + HO_2 \xrightarrow{k_4} H_2O + O_2 \tag{4}$$

TABLE 1. SUMMARY OF RESEARCH ON OZONE DECOMPOSITION IN WATER

Researcher	pH Range	Temp. range, °C.	Reaction order with respect to O_3
Alder & Hill	1 to 2.8	0 to 27	1
Stumm	7.6 to 10.4	1.2 to 19.8	1
Weiss	2 to 8	0	3/2
Kilpatrick et al.	0 to 6.8, 13	25	3/2,2
Raukas et al.	5.4 to 8.5	5 to 25	3/2
Rothmund & Burgstaller	2 to 4	0	2
Sennewald	5.3 to 8	0	2
Hewes & Davison	2 to 4	30 to 60	2
Hewes & Davison	6	10 to 50	3/2-2
Hewes & Davison	8	10 to 20	1

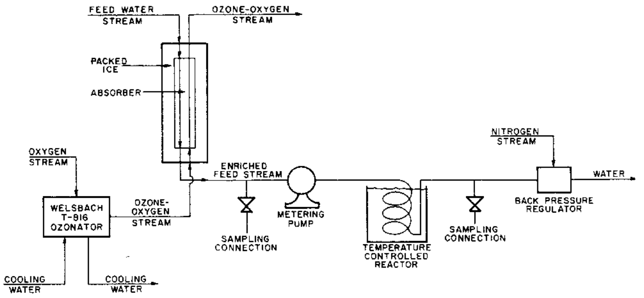

Fig. 1. Flow diagram of the continuous absorber-reaction system.

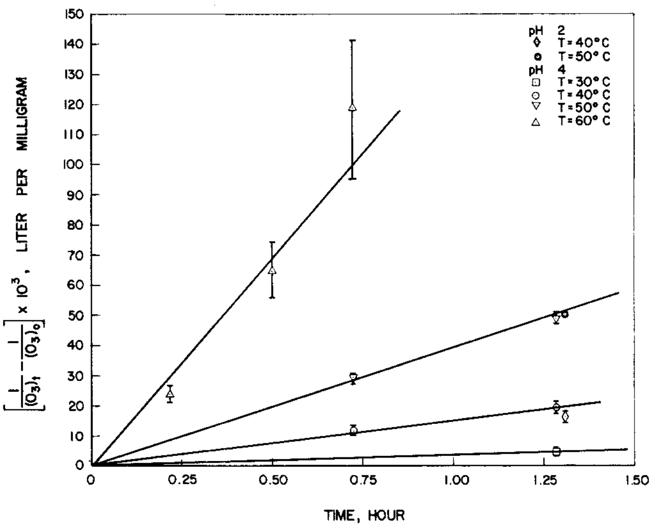

Fig. 2. Ozone decomposition in water solutions of pH 2 and 4 for a second-order reaction.

Steps (1) and (3), which are responsible for O_3 disappearance, were assumed to be relatively slow and rate controlling. Step (2) was assumed to represent an equilibrium. The rate equations are then solved under the assumption that

$$\frac{d(HO)}{dt} = 0; \quad \frac{d(HO_2)}{dt} = 0; \quad \frac{d(HO_3^+)}{dt} = 0 \quad (5)$$

which leads to

$$\frac{d(O_3)}{dt} = -3k_3\ (HO_2)(O_3) \quad (6)$$

which is first order with respect to O_3 and agrees with their spectrophotometric data. Using Step (2), Equation (6) becomes

$$\frac{d(O_3)}{dt} = -3k_3K^{1/2}\ (HO_3^+)^{1/2}\ (OH^-)^{1/2}\ (O_3) \quad (7)$$

which indicates a pH dependency for the rate of O_3 disappearance as determined spectrophotometrically, but little effect of pH was found for the total reducibles as measured iodometrically.

Kilpatrick et al. (*7*) studied ozone decomposition in aqueous perchloric acid solutions (the media used by Alder and Hill) and in highly alkaline solutions. They used iodometric, spectrophotometric, and manometric methods of analysis. Kilpatrick found that the iodometric and spectrophotometric methods gave the same rates of ozone decomposition in perchloric acid solutions. They reported the order of the reaction to be three halves. At high pH they found the rate to be second order. In phosphate arsenate buffer solutions at pH 6.8, they found the order to be three halves.

The results of Stumm (*11*) at higher pH's indicated that the reaction was first order with respect to O_3 and varied with pH such that

$$\frac{d(O_3)}{dt} = -k\ (OH)^{0.75}\ (O_3) \quad (8)$$

Rothmund and Burgstaller (*9*) studied the decomposition of ozone in a batch system at 0°C. from pH 2 to 4 and concluded that the reaction was second order. Sennewald (*10*) investigated the rate of ozone decomposition in a batch system at 0°C. from 5.3 to 8 pH. He found the reaction to be second order with the order independent of pH and salt content, but he reported the rate to increase with pH and postulated two simultaneous decomposition reactions.

Weiss (*12*) postulated a series of reactions similar to those of Alder and Hill which led to the following rate equation

$$\frac{-d(O_3)}{dt} = k_1\ (O_3)(OH^-) + k_2\ (O_3)^{3/2}(OH^-)^{1/2} \quad (9)$$

He then proceeded to argue that the data of Sennewald and Rothmund and Burgstaller could be represented by a three-halves-order reaction.

Raukas et al. (*8*) also reported a three-halves-order reaction between pH 5.4 to 8.5. They reported that the rate depends on pH and the electrical conductivity of the buffer solutions.

EXPERIMENTAL METHODS

The apparatus shown in Figure 1 is a continuous absorber-reaction system. It consisted of a 2-in. stainless steel absorber with a total length of 3 ft. packed with 2 ft. of ¼ in. × ⅛ in. pieces of glass tubing. The bottom section served as a collector and was equipped with a level gauge. A 5-gal. stainless steel feed tank pressured with air was used to feed water to the absorber. Both the feed tank and absorber were enclosed in ice-filled jackets to maintain low temperature and maximize the absorption of ozone.

Feed water to the absorber was controlled by a needle valve. The water from the absorber was pumped by a small metering pump into the reactor. The reactor consisted of ¼-in. stainless tubing of variable length coiled in a constant-temperature bath. The temperature in the bath was controlled to within ± 1°C. and the pressure in the reactor was maintained at 500 lb./sq. in. gauge by a gas-loaded back pressure regulator. The high pressure served to keep the dissolved ozone in solution at the reactor temperatures.

A Welsbach T-816 Ozonator produced an ozone-oxygen stream of approximately 60 to 80 mg. of ozone per liter. The concentration was measured by a model H-81 Welsbach Ozone Meter. The ozonator was operated at 8 lb./sq. in. gauge and at a flow rate of 1 to 2 liters/min. This gas was fed to the bottom of the absorber which was usually at a temperature of 10°C. and a pressure of 5 lb./sq.in. gauge. The ozone-oxygen stream from the absorber passed through a back pressure valve and outside the building. Water sample valves were located just before the metering pump and between the reactor and the gas loaded back pressure regulator.

After the system had reached steady state, about 2 hr., a sample was collected at the first sampling point. A sample was taken at the second sampling point after one space time—the time required to process one reactor volume of feed—had elapsed. There were some variations in the initial feed concentration, and in this way the initial and final samples of a run would be collected from the same material.

The pH of the feed water in the feed tank was not always the same as that out of the absorber and the reactor, and it was necessary to control the pH of the water with buffer

TABLE 2. OZONE DECOMPOSITION DATA

Run No.	pH	Temp., °C.	Time, hr.	Rate, ml./hr.	Ozone concentration, mg./liter In	Ozone concentration, mg./liter Out
1	8.05	10	0.2087	1,121.0	44.9	17.5
4	6.10	30	0.2135	975.4	47.8	26.5
5	6.20	40	0.2600	900.0	45.6	5.9
7	6.10	20	0.2790	838.5	46.1	37.3
11	6.20	10	0.4828	899.9	48.5	40.1
18	6.10	50	0.2087	1,121.0	53.3	4.8
25	3.90	30	1.2820	421.4	42.3	35.2
28	4.00	40	0.7235	746.8	51.8	32.6
29	4.00	50	0.7235	746.8	55.8	21.5
31	4.15	60	0.7235	746.8	50.2	7.3
33	2.10	50	1.3090	412.7	44.7	13.8
34	2.10	40	0.3090	412.7	47.0	24.8

solutions, if possible, at each pH. The buffer solutions which were used had to be inorganic, had to resist oxidation by ozone, and had to be insensitive to changes in temperatures. When the pH of the feed water was controlled without a buffer solution, it was necessary to have the pH in the feed tank below the desired value, since the pH of the water would be higher in the absorber than in the reactor. When there were buffers in the water, it was observed that the pH stayed the same from the absorber to the end of the reactor. A mixture of 1 M boric acid and 1 N sodium hydroxide was used as the buffer solution for the water solution of pH 8, while the buffer solution for pH 6 was 1 M potassium phosphate and 1 N sodium hydroxide. At pH's 4 and 2 it was necessary to control the pH without buffer solutions by using 1 M sulfuric acid, since there were no buffer solutions which would work in this range.

The ozone was determined iodometrically. In a report by Ingols et al. (*13*) it was shown that one molecule of ozone liberates equimolar amounts of oxygen and iodine when the pH medium is 9, according to the classical equation

$$O_3 + 2H^+ + 2I^- \rightleftarrows O_2 + I_2 + H_2O \qquad (10)$$

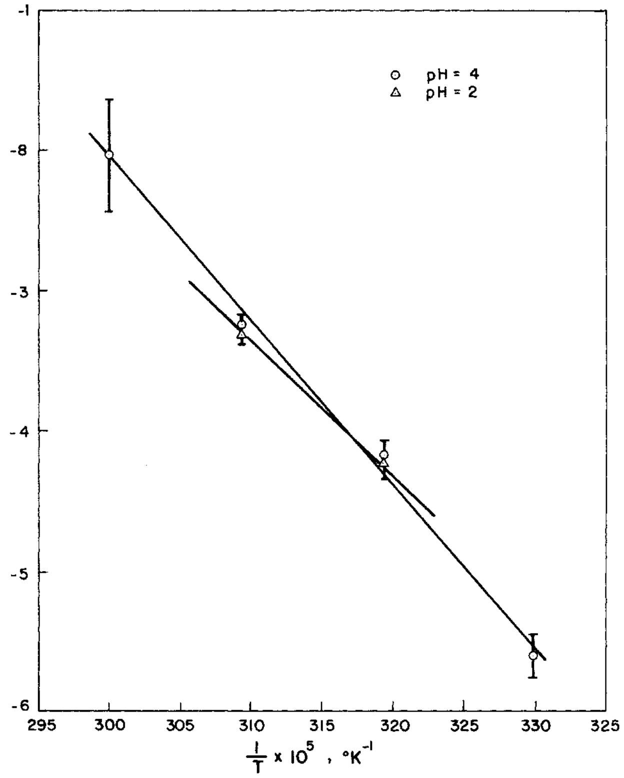

Fig. 3. Temperature dependency of ozone decomposition in water solutions of pH 2 and 4 for a second-order reaction.

Two percent potassium iodide was used to react with the ozone. Sodium carbonate was used as the buffer solution to keep the pH at about 9.5 while the sample was collected. After a portion of the feed stream had flowed into the potassium iodide trap, the aliquot was acidified with 10 ml. of 1 M sulfuric acid and was titrated with 0.005 or 0.025 N sodium thiosulfate solution with starch as the indicator. The end point was detected by a color change, the color going from blue-black to clear. The clear color had to remain for 1 min. before the titration could be assumed at the end point.

It would have been interesting to check the variation in iodometric and spectrophotometric results reported by Alder and Hill, but without an independent verification of the spectrophotometric procedure, absolute ozone concentrations are not known. At the high pH's and temperatures, any analytical procedure that does not immediately react with the residual ozone during sampling could not be used because of rapid ozone decomposition.

RESULTS OF OZONE DECOMPOSITION

Some of the experimental data are shown in Table 2. There are from 4 to 30 data points at each combination of

TABLE 3. THE SLOPE OF THE LINEAR EQUATIONS FOR THE RATE OF OZONE DECOMPOSITION IN WATER SOLUTIONS FOR FIGURES 2, 7, AND 4

pH	Temp., °C.	Reaction order	k, mg./(liter)(hr.)	Correlation coefficient
		Figure 2		
2	40	2.0	0.01186	0.9891
	50		0.03830	0.9999
4	30		0.00368	0.9974
	40		0.01514	0.9991
	50		0.03899	0.9997
	60		0.14946	0.9868
		Figure 7		
6	10	2.0	0.00491	0.9911
	20		0.01833	0.9971
	30		0.08114	0.9989
	40		0.21361	0.9913
	50		0.89979	0.9977
		Figure 4		
8	10	1.0	4.1735*	0.9936
	20		12.1520*	0.9994

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* k, (1/hr.)

pH and temperature, and each value in Table 2 is the average of 4 or 5 points. Rate constants for each set of data were calculated for a range of reaction orders from 0 to 2.5.

The order of the reaction of the ozone in water solutions was determined by the following two criteria: a plot of ln k versus $1/T$ for the data yields a straight line according to Arrhenius' law, and a plot of the data for a specific reaction order versus time yields a straight line. Since the data had to satisfy two straight lines, statistical parameters of the curves were needed to determine the order of the reaction. One statistical parameter used to determine the order of the reaction was the standard error of estimate for a simple linear regression of ln k on $1/T$ and the order plots. The other statistical parameter was the correlation coefficient for the same simple linear regression lines.

In Figures 2 to 7 each plotted point is the arithmetic mean of the dependent variable calculated from the four or five data at each condition. The variation in the dependent variable is shown by bars attached to the arithmetic mean point, and the width of the bars equals two standard deviations. In Table 3 the correlation coefficients and the linear equation coefficients are given for Figures 2, 4, and 7; Table 4 has these values for Figures 3, 5, and for the second-order line in Figure 6.

The rate of decomposition of ozone determined in water solutions at pH 2 was essentially the same as that of pH 4 at the same temperature. Figure 3 shows that the rate of decomposition between pH 2 and 4 is nearly independent of pH as measured by the iodometric method. This result agrees with the result of Alder and Hill (6), that the rate of ozone decomposition in aqueous solutions of pH 1 to 2.8 is independent of pH when the data are measured by the iodometric method.

At pH 2 and 4 the standard error of estimate for a simple linear regression line and the correlation coefficient for a second-order reaction were better than any value of the parameters found for other orders of reaction. In the calculation of the standard error of estimate and the correlation coefficient, it was necessary to weight the data for pH 4, because 15 of the 40 data points were taken at 60°C. and the experimental error was greater at this temperature than at the lower temperatures.

For pH 8 the standard error of estimate and the correlation coefficient for the Arrhenius equation had the best value for first-order reactions. The standard error of estimate for a first-order reaction at pH 8 was 0.089 and the correlation coefficient of the Arrhenius equation was 0.9870. In Table 3 the coefficients of the linear equation of Figure 4 are given along with the correlation coefficients for each experimental temperature at pH 8. Figure 5 shows the temperature dependency of the decomposition of ozone in water solutions of pH 8.

From the data taken at pH 6 it was impossible to deter-

TABLE 4. THE COEFFICIENTS OF THE LINEAR EQUATIONS FOR THE REACTION RATE CONSTANTS FOR THE DECOMPOSITION OF OZONE IN WATER SOLUTIONS

$\ln k = A^* (1/T) + B$

pH	Reaction order	A	B	Correlation coefficient
2	2.0	−9,768.5	26.965	0.9984
4	2.0	−11,631.0	32.849	0.9932
6	2.0	−11,571.0	35.581	0.9945
8	1.0	−8,480.0	31.422	0.9870

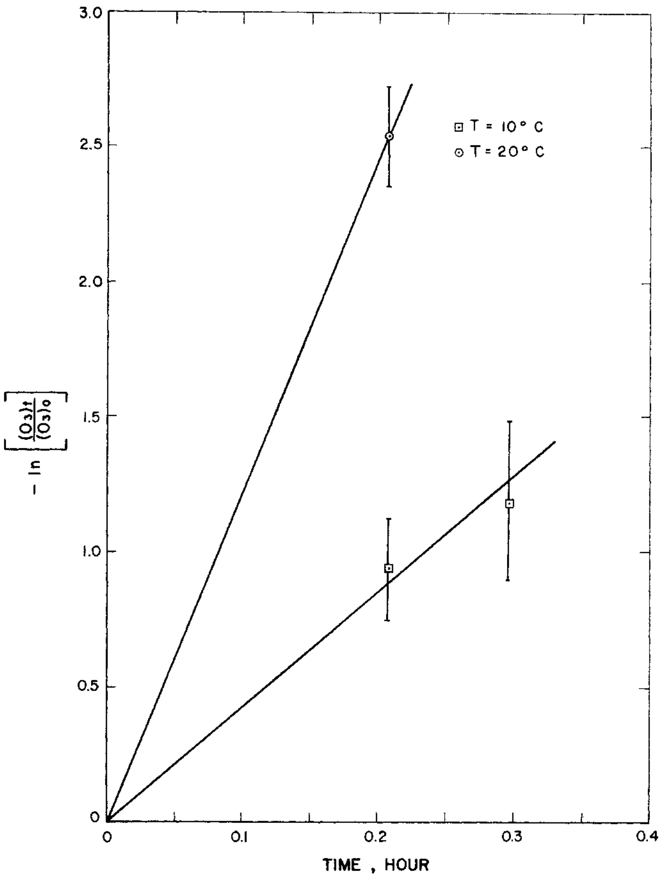

Fig. 4. Ozone decomposition in water solutions of pH 8 for a first-order reaction.

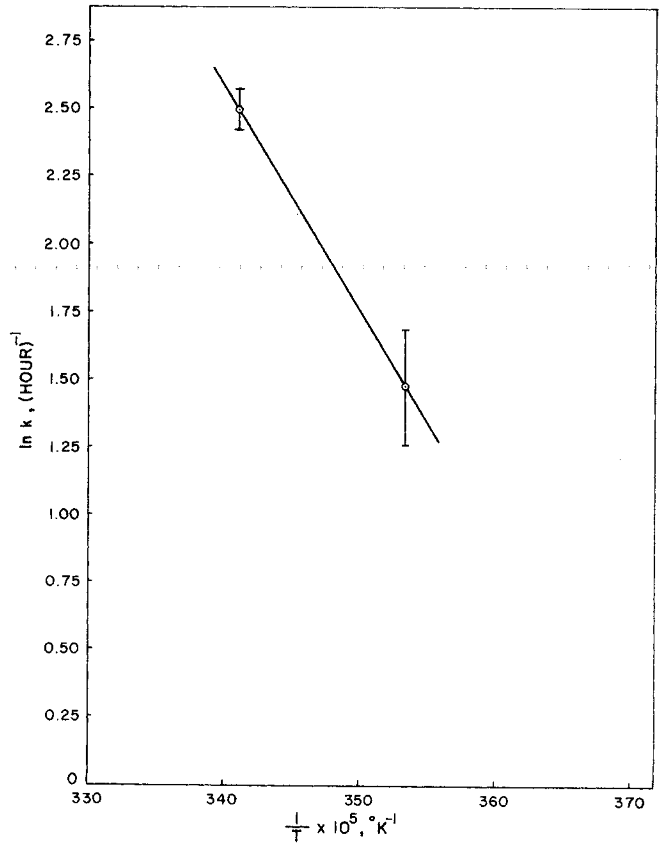

Fig. 5. Temperature dependency of ozone decomposition in water solutions of pH 8 for a first-order reaction.

mine the exact order of the reaction of decomposition. The standard errors of estimate and the correlation coefficients for pH 6 were approximately the same for the three-halves-, seven-fourths-, and second-order reactions. Figure 6 is a plot of the Arrhenius equation for various reaction orders between three-halves and five-halves. From this figure it is observed that the decomposition of ozone in water solutions of pH 6 could be taken as any order between second- and three-halves.

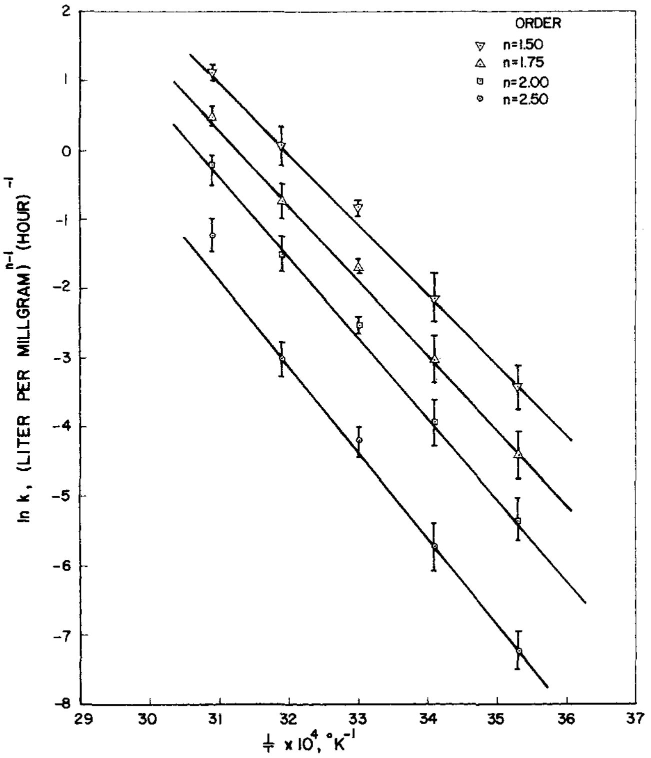

Fig. 6. Temperature dependency of ozone decomposition in water solutions of pH 6 for various reaction orders.

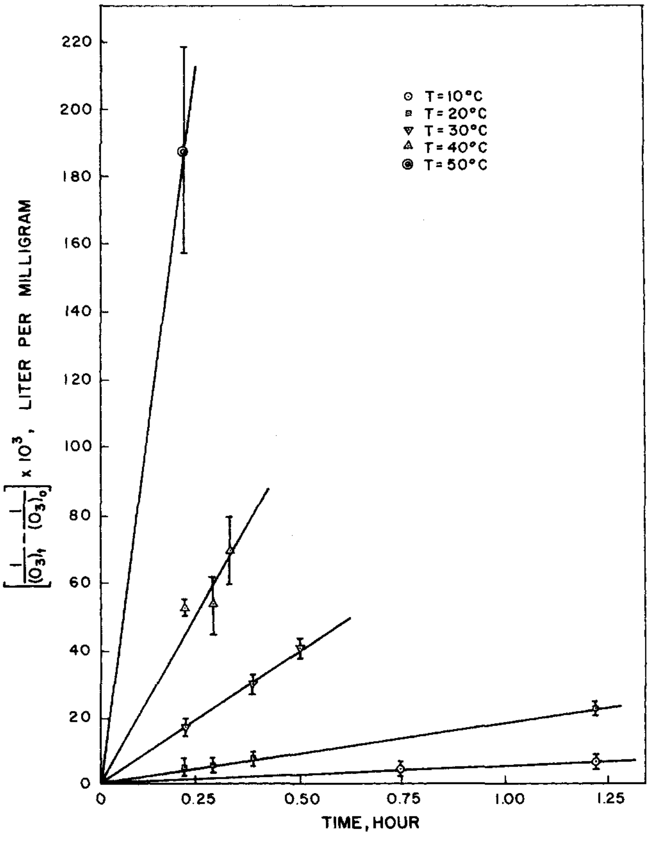

Fig. 7. Ozone decomposition in water solutions of pH 6 for a second-order reaction.

Figure 7 shows the plot of the experimental data for a second-order reaction for the decomposition of ozone in water solutions of pH 6. In Table 3 the coefficients of the linear equations of Figure 7 are given along with the correlation coefficients at pH 6 for each experimental temperature.

The indeterminate nature of the reaction order at pH 6 indicates that there is more than one significant reaction. The possibility that there was contribution from the pH insensitive second-order reactor found at pH 2 and 4 and the pH sensitive first-order reaction found at pH 8 was investigated. On comparing the second-order rate constants at pH 4 and 6, it is seen that those at pH 6 are an order of magnitude larger.

Stumm (*11*), whose data agree fairly well with ours, found that the first-order rate constant varied as $(OH)^{0.75}$. From this, the first-order rate constant could be determined at pH 6. The first-order rate calculated in this manner is of the same order of magnitude as the measured rates at pH 6. It seems likely therefore that the rate at pH 6 is a combination of the first-order reaction that is predominant at pH 8 with a higher order, but less pH sensitive reaction. A small contribution may exist from the pH insensitive second-order reaction that predominates at pH 2 and 4.

REACTION OF OZONE WITH ORGANICS IN WASTE WATER

As noted earlier, a number of studies have indicated that BOD and total carbon can be lowered by ozone. Most work has been at low temperature and not carried to completion, so an initial investigation was made to determine the conditions necessary for complete removal of organics as measured by the COD (chemical oxygen demand) test.

A batch system was constructed consisting of a 3-liter flask immersed in a constant-temperature bath. The sample was placed in the bath and brought to the desired temperature. Then the ozone-oxygen mixture from the Welsbach ozonator was bubbled through the water. Samples were withdrawn at intervals for COD analysis.

The water used was secondary effluent from the Bryan, Texas, sewage treatment plant. The water was filtered through Whatman No. 5 filter paper and then flocculated with ferric sulfate. After filtration the pH was reduced to 5.0 with HCl, and then the pH was lowered to 3.5 by the addition of a ferric sulfate solution containing 74.6 g. of ferric sulfate per liter of distilled water. Finally the pH was raised to 6.8 by the addition of a few drops of saturated sodium hydroxide solution. The clear liquid was decanted and again filtered.

The water was treated by flocculation prior to ozonation to remove all colloidol and suspended solids. Incidentlly, the COD was approximately halved by this treatment. In practical applications, a milder flocculation might be used, but it is a relatively cheap way of removing a portion of the organics.

Figure 8 shows the results of the COD analyses of samples from this system. The COD test was a modification of the dichromate reflux method of Moore (*14, 15*). It can be seen that the rate is much more rapid at elevated temperatures and apparently all the COD can be removed.

Table 5. Ozone-COD Reaction in the Continuous System

Concentrations in parts per million

Run No.	pH	COD entering absorber	COD leaving absorber	COD leaving reactor	Ozone leaving absorber	Ozone leaving reactor	Time in reactor, min.
1	7.9	36.6	19.7	19.3	24.0	4.9	9.6
2	7.5	36.8	22.5				
3	7.1	38.0	23.7				
4	8.0	30.2	17.7				
5	2.0	44.0	40.5				
6	2.0	46.9	38.7	38.0	74.3	45.9	9.6
7	7.6	33.0	19.0		74.3		

Since the solubility of ozone is actually much lower at the higher temperatures, it appears that the rate constant is even higher than indicated by the rate of COD disappearance.

With these favorable results in hand, the next step was to carry out the reaction in the continuous system in which both COD and ozone content could be measured in and out of the reactor. Sewage water treated as before was fed to the absorber in which presumably, because of the low temperature, the water would be saturated with ozone with little reaction taking place. The water from the absorber was then pumped into the reactor at 500 lb./sq.in. gauge. There it would be quickly heated to the reaction temperature in the long ¼-in. coil of tubing. The results of a number of runs are shown in Table 5.

The residence time of the water in the absorber was only about 7 min., yet at pH 7 to 8 nearly half the COD was destroyed. The temperature was only 10°C., so we would expect, according to Figure 8, only a small drop in COD. The reactor was at 50°C. Runs 2 to 5 were made using the absorber only, and it was noted that at pH 2, at which ozone decomposition is slow, the reduction of COD in the absorber was much less and the ozone in the absorber effluent much higher.

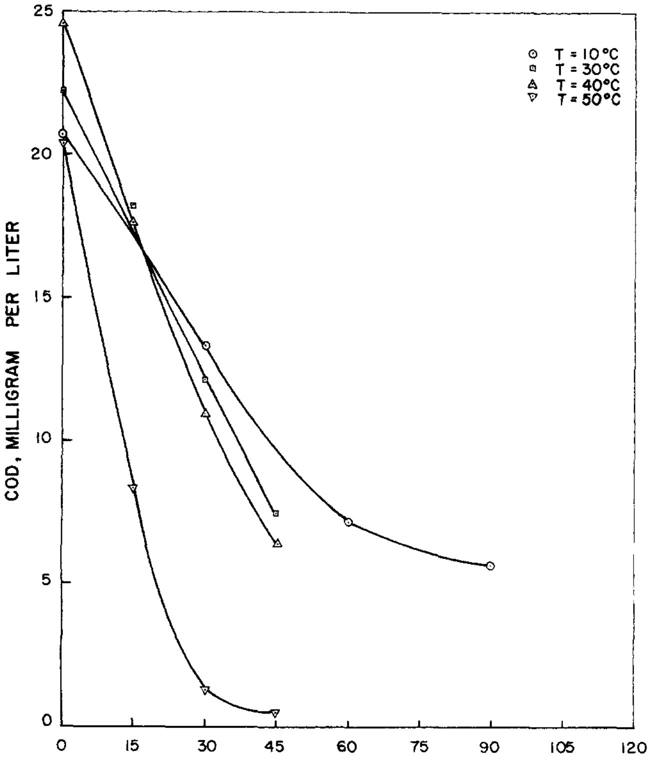

Fig. 8. The COD reduction of pretreated secondary municipal waste water effluents.

Run 6 is a complete run at 50°C. and pH 2. In spite of a high ozone content throughout, essentially no COD was removed in the reactor. Run 7 was made to determine the decomposition of ozone in the gas stream. In all the other runs about 1 liter/min. of oxygen containing about 74 mg./liter of ozone was fed to the absorber. In run 7 the rate was 0.85 liter/min. containing 54 mg./liter. The gas out of the absorber, after a very brief contact time, contained 24.5 mg./liter. In all seven runs about 1,140 cc./hr. of water were fed to the absorber. The quantity of ozone disappearing far exceeded what could dissolve in the water.

The discrepancy between the 10°C. batch data and those in the absorber was probably the result of much better gas-liquid contact in the absorber, resulting in a higher ozone decomposition rate. The ozone was present in such excess that anything that speeded its decomposition, such as higher pH and temperature, or better contact would increase the rate of organics removal.

A study of these data shows that the amount of COD removed is roughly proportional to the ozone decomposition rate rather than the concentration of undecomposed ozone. In the reactor, runs 1 and 6, the rate of ozone decomposition is about the same as that experienced in distilled water adjusted to the same pH's. The quantity of ozone actually decomposing in the reactor is negligible compared to that decomposing in the absorber. The efficiency of ozone utilization can only be about 3% of that decomposing, assuming one oxygen in ozone reacts. One can only conclude that the bulk of the COD reduction is due to reactions with decomposition products of ozone which are probably short-lived free radicals and ions. The higher rates obtained at 50°C. in the batch system may be due to greater ozone decomposition rather than higher rates in the subsequent reactions with COD.

A recent study by Huibers et al. (*16*) compliments this work in an interesting way. They contacted sewage effluent with ozone in a packed tower such that only a little if any excess ozone was present. In this way they obtained efficiencies of ozone utilization in excess of 100% when the ozone concentration was deficient and the COD was high, and about 20% at COD levels under 30 with some excess ozone. In our run 7, the efficiency is about 3%, but the ozone was added in 20-fold excess, resulting in very rapid but inefficient reaction.

If the results of runs 1 and 6 are taken literally, and this is very approximate since the difference in COD levels in and out of the reactor are not far from the accuracy of the measurements, we get efficiencies of about 4 and 7%, respectively. In these runs there was no excess ozone—in

TABLE 6. OZONATION OF WATER CONTAINING RESIDUAL AMINE

COD, mg./liter		Amine, mg./liter	
In	Out	In	Out
pH 4			
32.1	26.5	9.9	11.2
32.8	26.8	9.7	11.2
32.6	25.8	9.1	12.3
pH 7			
33.6	15.9	11.3	1.5
32.2	16.7	11.3	2.1
33.0	15.6	10.8	1.6

fact a deficiency—yet the utilization was very poor.

These facts cast considerable light on the probable mechanism for the ozone organic reaction. As postulated earlier, it probably begins with the decomposition of ozone, or its reaction with water, to form free radicals. However, since the radicals are highly reactive they will disappear rapidly through mutual reaction if their concentration is high as in our absorber runs.

Probably several kinds of free radicals are produced during ozone decomposition, but we will consider as an example the OH· radical.

$$RH + OH\cdot \rightarrow R\cdot + H_2O \qquad (11)$$

This could be followed by a process of autoxidation as described by Uri (*17*).

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (12)$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \qquad (13)$$

The hydroperoxides might also decompose as follows:

$$2\ ROOH \rightarrow H_2O + RO\cdot + RO_2\cdot \qquad (14)$$

$$ROOH \rightarrow RO\cdot + OH\cdot \qquad (15)$$

The chain terminating reactions would be

$$2RO_2\cdot \rightarrow \text{products}$$
$$RO_2\cdot + R\cdot \rightarrow \text{products}$$
$$2R\cdot \rightarrow \text{products}$$

It is seen that if the concentration of O_2 is high relative to the rate of free radical formation, reaction 12 et seq. will be favored, and even though the utilization of free radicals might be low, the overall efficiency relative to ozone might be high and could be over 100%.

In our absorber experiments the great excess of ozone gave a high level of free radicals. This led to rapid decrease in COD because of the primary reactions between free radicals and organics, but a low efficiency resulted because of the rapid reaction between free radicals.

Studies of hydrogen peroxide decomposition and its reaction in waste water by Bishop et al. (*18*) indicate a free radical mechanism also, but the efficiencies were also much higher than we have obtained with ozone. Again, however, there was little or no excess of peroxide, and the decomposition was slow, resulting in a low free radical concentration. They also report evidence of autoxidation. The hydrogen peroxide decomposition was catalyzed by metallic ions while no catalysts were present in the ozone system. It is likely that the autoxidation reactions were influenced by the catalyst. Therefore a complete investigation is needed of the interaction of pH, temperature, and various metallic ions in the regeneration of waste water by ozonation.

It is, of course, probable that many functional groups are attacked more readily than the carbon-carbon bond. Table 6 shows the results obtained by contacting water containing diisopropylamine in the absorber. The absorber temperature this time was 20°C. and the contact time about 10 min. The oxygen-ozone flow was 1.3 liters/hr. containing 65 mg./liter of ozone. There is an obvious discrepancy in the amine content at pH 4 but in either case little reaction occurs. At pH 7, on the other hand, half the COD and 80 to 85% of the amine is removed, confirming preferential attack on the amino group. This type of attack could be significant in water treatment where it is not necessary to remove all the COD but to render it innoxious.

CONCLUSIONS

It has been shown that the rate and order of the decomposition of ozone in water are pH dependent. The reaction rate of ozone with dissolved organic compounds seems to depend on the quantity of ozone decomposing rather than on the concentration of dissolved ozone, except insofar as the decomposition depends on concentration. It seems probable that free radicals formed by ozone decomposition are the principal reacting species. It has also been found that the efficiency of ozone utilization is increased by the presence of oxygen, which indicates that organic species, probably free radicals, formed by reaction with primary free radicals or other organic radicals can subsequently react with molecular oxygen. It appears that an economically attractive method of tertiary waste water treatment could result from the optimization of pH, temperature, ozone concentration, and oxygen to ozone ratio and contact time.

LITERATURE CITED

1. Buescher, C. A., and D. W. Ryckman, *Purdue Univ. Exp. Service Bulletin No. 109,* 251 (1962).
2. Evans, F. L., and D. W. Ryckman, *ibid. No. 115,* 141 (1963).
3. Marsh, G. R., and G. H. Panula, *Water Sewage Works,* **112,** 372 (1965).
4. Robeck, G. G., K. A. Dostal, J. M. Cohen, and J. F. Kreissl, *J. Am. Water Works Assoc.,* **57,** 181 (1965).
5. Bischoff, C., *Fortschr. Wasserchem. Ihren Grenzgeriete,* **9,** 121 (1968).
6. Alder, G. A., and G. R. Hill, *J. Am. Chem. Soc.,* **72,** 1884 (1950).
7. Kilpatrick, M. L., C. L. Herrick, and M Kilpatrick, *ibid.,* **78,** 1784 (1956).
8. Raukas, M. M., E. K. Siirode, and S. R. Kyulm, *Trudy Tallinskoga Politeknich. Inst. Ser. A,* **198,** 219 (1962).
9. Rothmund, V., and A. Burgstaller, *Monat. Chem.,* **34,** 665 (1913).
10. Sennewald, K., *Z. Phys. Chem. (Leipzig),* **A164,** 305 (1933).
11. Stumm, W., *Helvetica Chem. Acta.,* **37,** 773 (1954).
12. Weiss, J., *Trans. Faraday Soc.,* **31,** 668 (1935).
13. Ingols, R. S., R. H. Fetner, and W. H. Eberhardt, *Adv. Chem. Series No. 21,* **102** (1959).
14. Moore, W. A., R. C. Kroner, and C. C. Ruchhoft, *Anal. Chem.,* **21,** 953 (1949).
15. Dobbs, R. A., and R. T. Williams, *ibid.,* **35,** 1064 (1963).
16. Huibers, D. Th. A., R. McNabney, and A. Halfon, *Res. Contract Ser. Publ. No. CWR-20-7,* Federal Water Pollution Control Admin., Cincinnati, Ohio, (Apr. 1969).
17. Uri, N., "Autoxidation and Antioxidants," W. O. Lundberg, ed., Vol. 1, Chap. 2, Interscience, New York (1961).
18. Bishop, D. F., G. Stem, M. Fleischman, and L. S. Marshall, *Ind. Eng. Chem. Process Design Develop.,* **7,** 110 (1968).

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