

# RATE CONSTANTS OF REACTIONS OF OZONE WITH ORGANIC AND INORGANIC COMPOUNDS IN WATER—I

## NON-DISSOCIATING ORGANIC COMPOUNDS

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**Abstract**—Rate constants of reactions of ozone with non-ionized solutes, such as aliphatic alcohols, olefins, chlorosubstituted ethylenes, substituted benzenes and carbohydrates, have been determined from the absolute rates with which ozone reacts in the presence of various concentrations of these compounds in water. They have been tested by comparison with the relative rates by which pairs of these solutes are transformed by ozone. Different experimental methods have been developed to determine such rate constants in the range from  $10^{-2}$  to  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ . Interferences between the direct reactions of ozone and reactions due to its preliminary decomposition to secondary oxidants could be eliminated. The kinetics of all the reactions studied are first order with respect to ozone and solute concentration. The rate constants of many types of organic compounds in water are of the same order of magnitude as in organic solvents. Substituted benzenes, however, react in water about 100 times faster. They obey a linear free energy relationship with  $\rho = -3.1$  when based on  $\sigma_p^+$  values. Comparisons of rate constants with chemical structures of the reacting groups show that all reactions of ozone are highly selective and electrophilic. The kinetic data allow explanation of the chemical effects of ozone observed in water treatment practice.

### 1. INTRODUCTION

In many countries ozone is widely used for treatment of drinking water to improve taste, color, disinfection, filtration characteristics or even biodegradability of impurities. It is also applied for the oxidation of specified compounds in industrial waste-waters or exhaust-gas scrubbers. From these applications ozone is known to be a highly selective oxidant and many types of ozonation products are observed or postulated which are oxidized further only upon very prolonged ozonation (for reviews see Bailey, 1972; Gilbert, 1978; Oehlschlager, 1978; Rice, 1982). Therefore, in order to evaluate advantages and risks of ozonation processes, kinetic data are needed to predict what products will remain in the water after specified durations of ozonations. Kinetic data are also of importance for learning more about the environmental behaviour of ozone when absorbed in natural aquatic systems.

In spite of the widespread practical application of ozonation only a few rate constants for reactions of ozone with substances dissolved in water have been published so far: These are for formic acid (Taube, 1941), nitrilotriacetate (Games & Staubach, 1980), ammonia (Hoigné & Bader, 1978), nitrite, sulfur dioxide, and hydrogen sulfide (Penkett, 1972), bromide (Taube, 1942), cobaltous ion (Hill, 1949), and  $\text{OH}^-$  and  $\text{H}_2\text{O}_2$  ( $\text{HO}_2^-$ ) (Stachelin & Hoigné, 1981). The many other reaction-rate constants quoted for non-aqueous solvents can however not directly be applied in aqueous systems.

In this study (Part I) we focus on measurements of the direct reactions of molecular ozone with solutes which do not dissociate. Reaction-rate constants for the reactions of ozone with solutes which can dissociate and form ionic species will be presented in Part II (Hoigné & Bader, 1983a) and those with inorganic substances in Part III (Hoigné & Bader, 1983b).

Oxidation reactions initiated by ozone in water are generally rather complex; in water, only part of the ozone reacts directly with dissolved solutes. Another part may decompose before reaction. Such decompositions are catalysed by hydroxide ions and other solutes. Highly reactive secondary oxidants, such as  $\text{OH}^\cdot$  radicals, are thereby formed (Hoigné & Bader, 1976; Stumm, 1954; Taube & Bray, 1940). These radicals and their reaction products can additionally accelerate the decomposition of ozone (Stachelin & Hoigné, 1981; Taube, 1941). Consequently radical type chain reactions may occur which consume ozone concurrently with the direct reaction of ozone with dissolved compounds. The situation is depicted in Fig. 1. In ground and surface waters used for drinking waters (pH about 7–8) the two reaction pathways can be of comparable importance (Hewes & Davison, 1971; Hoigné & Bader, 1976, 1978a–d; Hoigné, 1982). These pathways are, however, regulated by very different parameters and they generally lead to different oxidation products. In order to elucidate oxidations initiated by ozonation, the direct ozonation of solutes must therefore be distinguished from other (secondary) oxidation reactions and studied separately.

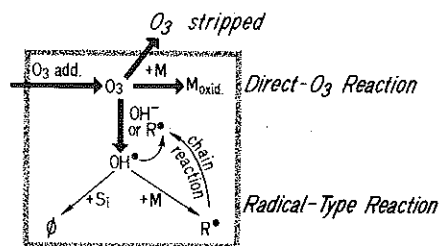
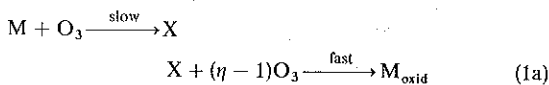


Fig. 1. Scheme of reactions of ozone added to an aqueous solution. M = solute;  $M_{\text{oxid}}$  = oxidized solute;  $S_i$  = free radical scavenger  $i$ ;  $\emptyset$  = products which do not catalyze the ozone decomposition; R = free radicals which catalyze the ozone decomposition.

## 2. REACTION MODEL

For the direct reaction of ozone with a solute M we may write:



or



where  $\eta$  is a stoichiometric factor for the number of ozone molecules consumed per molecule M transformed to  $M_{\text{oxid}}$ . Its value depends on the type of solute M and possibly on the concentration of ozone and other reaction parameters. It lies typically in the range between 1 and 5 (for solutes tested for this publication, between 1 and 2.5), X is the primary intermediate formed by the rate determining step. This intermediate may consume  $\eta - 1$  further ozone molecules in fast succeeding reactions and be thereby oxidized to  $M_{\text{oxid}}$ .  $M_{\text{oxid}}$  is a relatively stable product which consumes no further ozone during the measurement. Because the rates of reactions of ozone with different oxidation products may differ by many orders of magnitudes, it is generally easy to discriminate final products ( $M_{\text{oxid}}$ ) from short living intermediates (X) which consume further ozone.

### Absolute rate constants for ozone consumption

If the rate of direct reaction of ozone with dissolved substances is assumed to be first order with respect to ozone concentration, the rate law can be formulated as:

$$-d[O_3]/dt = k_{O_3}[O_3][M]^n \quad (2)$$

where  $k_{O_3}$  is the rate constant for the consumption of ozone by all reactions leading from M to  $M_{\text{oxid}}$ .

When M is present in large excess the reaction rate becomes pseudo-first order. For such a reaction proceeding in a batch-type reactor, integration of equation (2) yields:

$$-2.3 \log ([O_3]_t/[O_3]_0) = k_{O_3} \cdot [M]_0^n \cdot t \quad (3)$$

for  $[O_3]_0 \ll [M]_0$

where  $[O_3]_0$  and  $[O_3]_t$  are concentrations of ozone at time zero and time  $t$  respectively. If  $\tau_{O_3}$  denotes the time within which the concentration of ozone is reduced by the factor  $e$ , we may write for the pseudo-first order rate constant by which ozone becomes consumed,  $1/\tau_{O_3}$ :

$$1/\tau_{O_3} = k \cdot [M]_0^n \quad (4)$$

or

$$\log (1/\tau_{O_3}) = \log k + n \cdot \log [M]_0 \quad (5)$$

A plot of  $\log (1/\tau_{O_3})$  vs  $\log [M]_0$  yields a line from which  $k_{O_3}$  can be determined. This plot gives a straight-line relationship if  $k_{O_3}$  (that means also the stoichiometric factor  $\eta$ ) is independent of  $[M]_0$ . The slope of these lines becomes 1.0 if the reaction is first order with respect to the solute concentration (i.e.  $n = 1$ ).

### Relative reaction-rate constants

Because  $\eta$  molecules of ozone react per molecule of M, the rate of disappearance of the solute M is  $\eta$  times slower than the rate of ozone consumption [cf. equation (2)] and  $k_{O_3}/\eta$  becomes the rate-constant for M reacting with ozone. In cases where different types of solutes ( $M_1, M_2, \dots$ ) react with ozone in competition, we may write for the relative residual concentrations of M at time  $t$  for the case of a batch-type reactor:

$$\log ([M_1]_t/[M_1]_0) / \log ([M_2]_t/[M_2]_0) = (\eta_1/\eta_2) \cdot k_2/k_1 = k_{\text{rel}} \approx k_2/k_1 \quad (6)$$

When similar types of solutes are compared,  $\eta_1/\eta_2$  is about unity and the approximation included on the right hand side of equation (6) can be used for many practical applications.

## 3. EXPERIMENTAL

Stock solutions of aqueous ozone were prepared as described by Bader & Hoigné (1981). pH adjustment in the reaction bottles was made by adding sodium hydroxide/phosphoric acid buffers so that the total phosphate concentration in the final solution was 0.05 M. Organic compounds were of reagent grade and used without further purification except that the stabilizer present in diethylether was extracted by 0.1 M sodium hydroxide.

### Indigo Reagent for the determination of ozone

The Indigo Reagent contained  $0.62 \text{ g l}^{-1}$  (1 mM) potassium indigotrisulfonate (Riedel de Haen) in 0.02 M phosphoric acid. The Indigo Reagent was diluted before use. The amount added to the reaction bottles was adapted to suit the maximal amount of residual ozone expected to occur within the series (0.5–50  $\mu\text{M}$ ) (Hoigné & Bader, 1980; Bader & Hoigné, 1981).

### Spectrophotometer

A Beckman DK 2A Recording Spectrophotometer was used for most measurements. Special cell holders allowed thermostating. Cell path-lengths were from 0.5 to 5 cm. The cells had to be left in position in the instrument during filling and flushing, when the residual ozone was determined by the indigo method.

### Procedures to determine absolute rate constants

The absolute rate constants were measured by several different procedures. In all cases aqueous solutions of M and buffer and scavenger were first pipetted into u.v. cells or into other flasks used as "reactors". The reaction was started by adding a solution of ozone below the liquid level by injection, yielding thorough mixing without entrainment of air. Then, the concentration of ozone in the solution was followed vs time. Measurements were repeated using varied initial concentrations of reactants and at different pH values.

For many solutes the change in ozone concentration was directly measured spectrophotometrically in thermostated u.v. cells (1 or 5 cm path length,  $[O_3]_0 = 2\text{--}300 \mu\text{M}$ ) by recording the absorbance at 258 nm. In these experiments volumes were chosen to minimize headspace in the u.v. cells. The cells were kept closed during the measurement. By this method half lives ranging from 5 up to a few thousand seconds could be determined. Figure 2(A) gives a graphical representation of the results of such measurements.

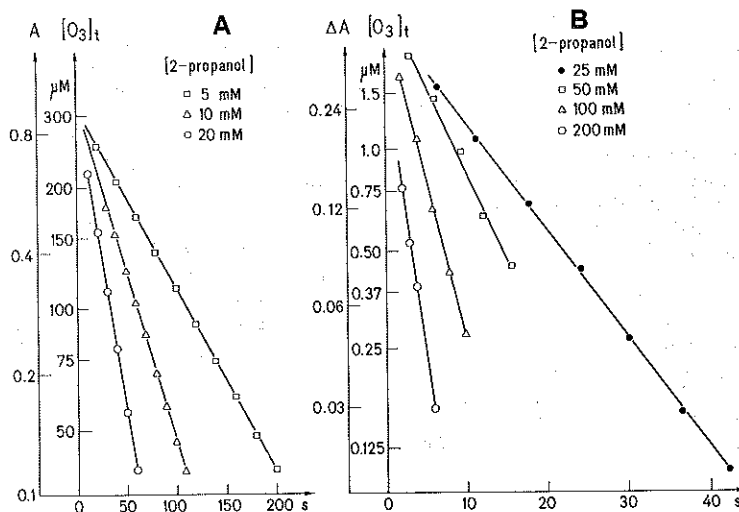


Fig. 2. Concentration of  $[O_3]$  vs time in presence of an excess of 2-propanol. (A) Direct measurement of  $[O_3]$  by recording its u.v. absorbance at 258 nm in a 1 cm u.v. cell. (B) Measurement of  $[O_3]$  in series of samples by the indigo method.  $\Delta A$  is the change of absorbance (600 nm) due to the residual ozone in the samples in a 5 cm u.v. cell.

Some solutes, such as aromatic hydrocarbons, interfere with the spectrophotometric determination of ozone at 258 nm. For these solutes the concentration of residual ozone as a function of time was measured by the indigo method. This method is based on the decolorization of an aqueous indigo-trisulfonate reagent by ozone observed at 600 nm (Hoigné & Bader, 1980; Bader & Hoigné, 1981). The Indigo Reagent reacts immediately with all residual ozone ( $k > 10^7 M^{-1} s^{-1}$ ) and ozone concentrations as low as 0.5  $\mu M$  can be determined with an accuracy of better than 10%. In each series of measurements the measured values of the residual concentration of ozone decreased with extended reaction time to zero. This indicated that no ozonation products formed (such as peroxides) from any solutes applied disturbed the determination of residual ozone when this was performed with this indigo method.

Two different procedures based on the indigo method were used: (i) For slowly reacting systems ( $\tau_{O_3} > 100$  s), a 1 l. Erlenmeyer flask was used as a reactor. The contents of the flask (1 l.) were stirred by a magnetic bar during ozone addition and the flask closed after the ozone was added. At regular intervals, which ranged from 20 to 200 s, 5–10 samples were withdrawn using a piston controlled pipette. These samples were transferred into 25 ml bottles containing 2.00 ml of buffered Indigo Reagent. By this procedure the concentration of the residual ozone could be measured by determining the decolorization caused by the transferred solution. (ii) In case of fast reactions with  $\tau_{O_3} < 100$  s, series of about ten 25 ml bottles were used as reactors. Solute and buffers were added to these bottles and then ozone stock-solution was added using a piston controlled pipette. Stirring was interrupted after 5 s. After different time intervals the reactions in the individual bottles were stopped by fast addition of 1.0 ml of Indigo Reagent from a piston controlled pipette whilst stirring was restarted. The residual absorbance of the Indigo Reagent was measured. An example of the results of this method is given in Fig. 2(B). Data from samples stopped after more than 3 s were not influenced by the rate of mixing. This was checked by comparing the results found for very fast reacting solutes under widely varied reaction conditions (see e.g.  $NO_2^-/HNO_2$  system vs pH in Part III).

All methods used gave consistent results. An example is presented in Fig. 3.

Reactions carried out in u.v. cells were thermostated at  $20.0 \pm 0.5^\circ C$ . The other experiments were performed at  $23 \pm 0.5^\circ C$ . For experiments performed to determine temperature effects on the rate constants, the temperature was controlled to  $\pm 0.5^\circ C$ .

Solute concentrations  $[M]_0$  were chosen to give half lives of ozone in the range of 1–1000 s. Generally, the ratio of  $[M]_0$  to  $[O_3]_0$  added was at least  $10 \text{ mol mol}^{-1}$  to ensure that the reactions would stay pseudo-first order. Series of measurements were performed within which the concentration of M was varied over as wide a range as feasible. This range usually covered a factor between 5 and

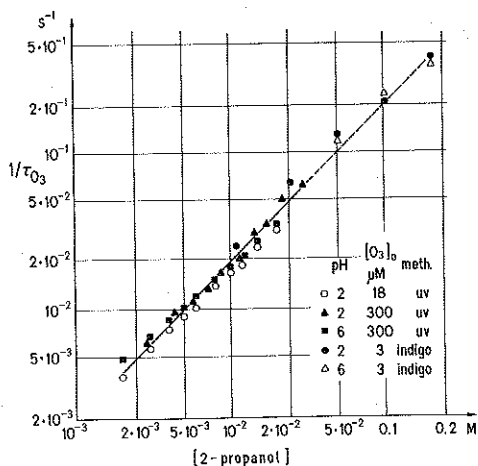


Fig. 3. Comparison of results from different experimental methods applied for the determination of the rate of ozone consumption ( $1/\tau_{O_3}$ ) vs conc. of 2-propanol (slope of line = 1.0).

20 except for solutes having low solubility or a high reaction rate constant. In order to certify that the kinetics of ozone consumption were not disturbed by the presence of rapidly reacting impurities, tests were included for each solute using small ratios of  $[M]_0$  to  $[O_3]_0$  or on pre-ozonized samples.

Most measurements reported in this Section were performed at pH 2. Additional measurements at higher pH values were made to test for interferences by catalytic decomposition of ozone. Such interferences would show significant pH dependence (cf. Fig. 1 and Hoigné & Bader, 1977).

#### Procedure to determine relative reaction-rate constants

In solutions containing  $0.1\text{--}10\text{ mg l}^{-1}$  of different pairs of solutes, the relative residual concentrations of these solutes were measured after all of the ozone added had reacted [see equation (6)]. In each series of experiments the relative initial solute concentrations were varied, e.g. from 1:3 to 3:1. Different amounts of ozone were added to the individual samples of the series. The range of ozone dosage was chosen to achieve 20–80% depletion of the concentrations of the solutes to be compared. The procedures corresponded with those applied by Hoigné & Bader (1976), except that in the present work gas-chromatographic determinations of the residual concentrations of solutes were made on pentane or benzene extracts or on head-space samples (Hoigné & Bader, 1979b).

A pair of reference substances was always included in the solutions of the compounds to be measured in order to test for the absence of interactions by secondary oxidants. Thereby reference pairs were used for which the  $k_{rel}$  value was known from independent series of measurements. Furthermore, most measurements were made on samples to which a large excess of propanol or *t*-butanol has been added in order to scavenge OH radicals and thereby quench possible OH free-radical type reactions.

#### Methods to inhibit the decomposition of ozone

The determination of reaction-rate constants of ozone was often limited by the concurrent decomposition of ozone (see Fig. 1). General information on the magnitude of the rate of this decomposition and its dependence on pH or radical scavengers is given in Fig. 4. In the examples used for this illustration, the half life of the ozone was only limited by the rate of decomposition. Based on this and previous information (Hoigné & Bader, 1976, 1977), the rate of decomposition of ozone was lowered by decreasing the pH of the solution, and by adding *n*-propanol, tert-butanol or methylmercury (for solutions of pH above 4), or

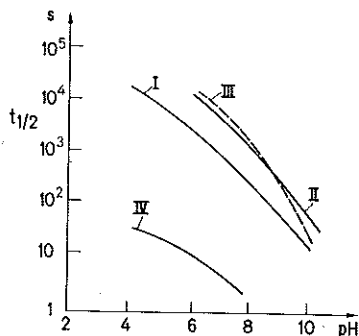


Fig. 4. Half-life of ozone in aqueous solutions.  $[O_3]_0 = 300\ \mu\text{M}$ . Buffer: 0.05 M phosphoric acid/sodium phosphate. I—no other solute; II—sodium bicarbonate,  $\Sigma[\text{CO}_2] = 2\text{ mM}$ ; III—0.3 mM methyl mercury hydroxide; IV—0.08 mM benzene.

bicarbonate (for pH above 7). The concentrations of these scavengers were kept as low as possible. They are tabulated for each series of measured reaction-rate constants. Cases in which the concurrent decomposition of ozone disturbed the measurement of reaction-rate constants were identified by tests showing that the reactions deviated from first order with respect to ozone or solute concentrations or that they depended on pH or on increased scavenger concentrations.

#### Determination of stoichiometric factors

The stoichiometric factors of ozone reacting with a few different solutes were determined. In these experiments ozone dosages necessary to oxidize between 30 and 70% of the dissolved compound M were used. The depletion of M was measured by gas-chromatographic methods after all ozone reacted.

## 4. RESULTS

### Reaction-rate constants for consumption of ozone by solutes

A semi-logarithmic plot of ozone concentration vs time was linear in all cases which met the criteria described in the experimental part. Such linearities could be tested over a range until the residual ozone was 10% of its original concentration. This limitation was due to the instrumental type of the ozone analysis applied and the condition that the relative concentration of the residual ozone could still be determined with an accuracy of at least 10%. However, tests performed on a few selected systems showed that the slope of these lines did not change even when the initial concentration of ozone was varied by a factor 100 (see e.g. Fig. 3). The  $1/\tau_{O_3}$  values defined for pseudo-first order reactions [see equation (3)] could therefore directly be determined from the slopes of these plots.

In all acceptable series of measurements log-log plots of  $1/\tau_{O_3}$  vs the solute concentration gave linear relationships [cf. equation (5)]. Results of a comprehensive study are given in Fig. 3 and, further examples are presented in Fig. 5 and in Part II. The slopes  $n$  of the lines never significantly differed from  $1.0 \pm 0.1$ . These results indicate that the reactions are first-order also in solute concentration. Whenever deviations have been observed in preliminary series of measurements, these could be circumvented in later series by using a lower pH or by adding a higher concentration of a free radicals scavenger. (In solutions containing benzene or some of the substituted benzenes, the radical-type chain reaction sometimes led to significant rates of decomposition of ozone already at pH values above 2.5.) In case of most aliphatic compounds, however, the pH range giving consistent results could be extended to values above 5 and sometimes even up to 8. Second order reaction-rate constants could therefore be determined for all solutes by dividing the  $1/\tau_{O_3}$  values by the concentration of the solute applied. The results are listed in Tables 1–4. There the rate-constants which had been tested most extensively and which can be recommended as reference values are underlined.

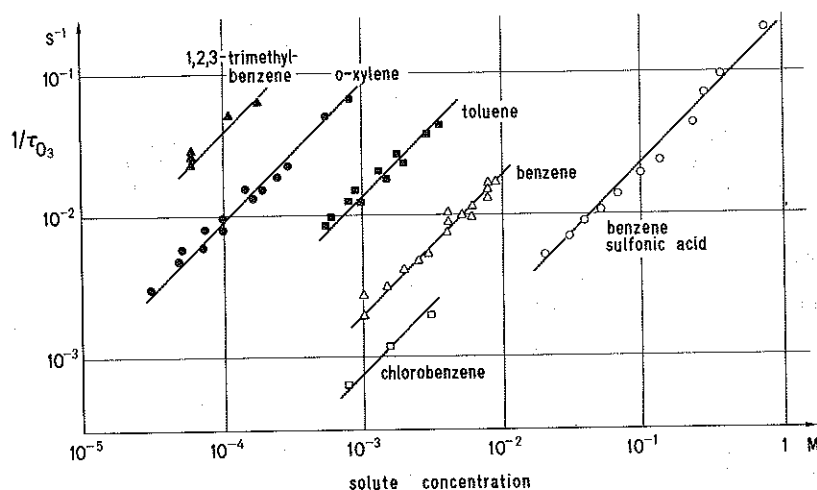


Fig. 5. Rates of ozone consumption measured ( $1/\tau_{O_3}$ ) vs the conc. of different substituted benzenes (slope of lines = 1.0) (for numerical results see Table 1).

To estimate the accuracy of the rate-constants the following points had to be considered: (i) At extended times of ozonation, such as required for measurements on slowly reacting solutes present at low concentrations, concurrent losses of ozone may become significant. (ii) Small amounts of impurities present in

the reagent solutions could add to the rate of ozone consumption if exorbitant ratios of concentrations of M to ozone are used. (iii) If M has a high volatility or a low solubility, its concentrations may change by evaporation or adsorption processes. Therefore the limits of confidence given in Tables 1-4 are estimates

Table 1. Reaction-rate constants of substituted benzenes\*

Solute	mM	pH	Scavenger	mM	$k_{O_3}$ ( $M^{-1}s^{-1}$ )	(N)†
Nitrobenzene	5/10	2	<i>t</i> -BuOH	50-1000	$0.09 \pm 0.02$	(2)
Benzene sulfonate ion	10-800	1.7-2	<i>t</i> -BuOH	50-800	$0.23 \pm 0.05$	(12)
1,2,4-Trichlorobenzene	0.05	2	<i>t</i> -BuOH	10	$\leq 1.6$	(1)
1,4-Dichlorobenzene	0.05	2	<i>t</i> -BuOH	0.5	$\leq 3$	(1)
Chlorobenzene	0.8-3	2	PrOH	1	$0.75 \pm 0.2$	(3)§
Methyl benzoate	1000	2	<i>t</i> -BuOH	100	$1.1 \pm 0.3$	(1)§
Benzoate ion	10-100	5	<i>t</i> -BuOH	100-1000	$1.2 \pm 0.2$	(5)
Benzene	1-10	1.7-3	—	—	$2 \pm 0.4$	(27)
Benzaldehyde	2-10	1.7	—	—	$2.5 \pm 0.5$	(4)
Iso-Propylbenzene	0.14	2.0	<i>t</i> -BuOH	100	$11 \pm 3$	(1)§
Toluene	0.4-4	1.7	—	—	$14 \pm 3$	(12)
4-Nitrophenol‡	0.01-14	1.7	PrOH	—	$< 50$	(see Part II)
Ethylbenzene	0.25-1	2.0	<i>t</i> -BuOH	100	$14 \pm 4$	(3)§
<i>o</i> -Xylene	0.03-0.8	1.7-5	—	—	$90 \pm 20$	(20)
<i>m</i> -Xylene	0.2-0.5	2.0	<i>t</i> -BuOH	1	$94 \pm 20$	(5)
<i>p</i> -Xylene	0.2-0.5	2.0	<i>t</i> -BuOH	1	$140 \pm 30$	(5)
Anisole	0.05-0.8	2	PrOH	1	$290 \pm 50$	(10)
1,2,3-Trimethylbenzene	0.06-0.2	1.7	—	—	$400 \pm 100$	(7)
1,3,5-Trimethylbenzene	0.05-0.1	1.7	—	—	$700 \pm 200$	(6)
4-Chlorophenol	0.1-0.5	2	PrOH	1	$600 \pm 100$	(see Part II)
Phenol‡	0.01-0.1	1.7-2	PrOH	1	$1300 \pm 300$	(see Part II)
Salicylic acid‡	0.1-1	1.3-3	<i>t</i> -BuOH	4	$< 600$	(see Part II)
Salicylate ion	0.03	4-7	<i>t</i> -BuOH	4	$(30 \pm 10) \cdot 10^3$	(see Part II)
Resorcinol‡	0.003	2	PrOH	—	$> 300,000$	(see Part II)
Naphthalene	0.002-0.14	2	<i>t</i> -BuOH	1	$3000 \pm 600$	(9)

\*All measurements by indigo method.

†Number of measured rate curves of  $[O_3]_t$  vs time.

‡Rates of reactions of deprotonated species becomes already significant at very low pH values. See Part II also for more extended series.

§Reaction-rate constants determined primarily by relative measurements (references: benzene; toluene; *o*-xylene).

Table 2. Reaction-rate constants of substituted ethylene

Solute	mM	pH	Method¶	Scavenger mM	$k_{O_3}$ ( $M^{-1}s^{-1}$ )	(N)†
Tetrachloroethylene	0.7	2.0	u.v.	—	<0.1	(2)
Trichloroethylene	0.06–0.6	2.0	u.v.	—	$17 \pm 4$	(10)
cis-Dichloroethylene¶	0.06–0.2	2.0	u.v.	—	<800	(4)
1,1-Dichloroethylene	0.04–0.4	2.0	u.v.	—	$110 \pm 20$	(10)
Maleic acid	0.1–0.7	2	I	<i>t</i> -BuOH 1.5	$\sim 10^3$	(10)
Fumaric acid	0.1–1	2	I	<i>t</i> -BuOH 1.5	$\sim 6 \cdot 10^3$	(6)
<i>trans</i> -Dichloroethylene	0.03–0.1	2.0	u.v.	<i>t</i> -BuOH 1	$5.7 \pm 1.0 \cdot 10^3$	(5)
1-Hexene-3-ol	$3 \cdot 10^{-3}$	2.0	u.v.	<i>t</i> -BuOH 4	$\sim 1.0 \cdot 10^5$	(1)
Allylbenzene	$3/4 \cdot 10^{-3}$	2.0	I	PrOH 2	$1.2 \pm 0.4 \cdot 10^5$	(2)
1-Hexene-4-ol	$3 \cdot 10^{-3}$	2.0	u.v.	<i>t</i> -BuOH 4	$\sim 1.8 \cdot 10^5$	(1)
Styrene	$7 \cdot 10^{-3}$	2.0	I	<i>t</i> -BuOH 1	$\sim 3 \cdot 10^5$	(1)

†See Table 1.

¶Determination of ozone by: I = indigo method; u.v. = u.v. absorbance at 258 nm.

‡Contaminated with about 5% *trans*-dichloroethylene.

Table 3. Reaction-rate constants of substituted alkanes¶

Solute	mM	pH	$k_{O_3}$ ( $M^{-1}s^{-1}$ )	(N)†
1-Propylamine		2	<0.01	(2)
1-Butylamine		2	<0.02	(1)
tert-Butanol	600	2/6	$\sim 0.003$	(2)
Methanol	600	2/5	$\sim 0.024$	(4)
Ethanol	6–60	2	$0.37 \pm 0.04$	(10)
1-Propanol	6–60	2	$0.37 \pm 0.04$	(10)
1-Octanol	0.8–1.4	2	$\leq 0.8$	(3)
1-Butanol	1–10	2	$0.58 \pm 0.06$	(9)
2-Propanol	2–30	2/6	$1.9 \pm 0.2$	(30)
Cyclopentanol	2–20	2	$2.0 \pm 0.2$	(10)
Formaldehyde	70–600	2	$0.1 \pm 0.03$	(8)
Acetaldehyde	20–100	2	$1.5 \pm 0.2$	(3)
Propanal	30–300	2	$2.5 \pm 0.4$	(3)
<i>n</i> -Octanal	0.1–0.2	1.8–5	$8 \pm 0.8$	(11)

†See Table 1.

‡All measurements by direct u.v. method.

based on experience accumulated from measurements made using various conditions or procedures and not from the precision achieved within individual series.

Rate constants determined at different temperatures are presented in Fig. 6.

#### Relative reaction-rate constants for elimination of solutes

Two examples of results of relative rates ( $k_{rel}$ ) with which different compounds competed with each other for being eliminated by ozone [cf. equation (6)] are presented in Table 5. Further results are presented in Part II (Fig. 8). Only those systems of solutes were evaluated in which no evidence of interferences by radical-type reactions resulted when tested as described in the experimental part.

#### The stoichiometric factors

All values of  $\eta$  determined ranged from 1 (for olefi-

nic compounds) to 2.5 (for aromatic hydrocarbons). Individual results will not be discussed in this paper because they do not significantly influence the interpretation of the kinetic data presented. Moreover, the yield factors agree well with those already discussed in many other publications.

## 5. DISCUSSION

### Methods

All results correspond with the assumption that the rate laws for the reactions of ozone with aqueous solutes are first order with respect to both ozone and solute concentrations. Therefore the kinetic data can best be expressed by second-order reaction rate constants based on the equation:

$$-d[O_3]/dt = k_{O_3}[O_3]^{1.0}[M]^{1.0}.$$

It has also been observed that these  $k_{O_3}$  values neither change significantly within the ranges of the ratios of  $[M]_0/[O_3]_0$  used in the experiments nor with the

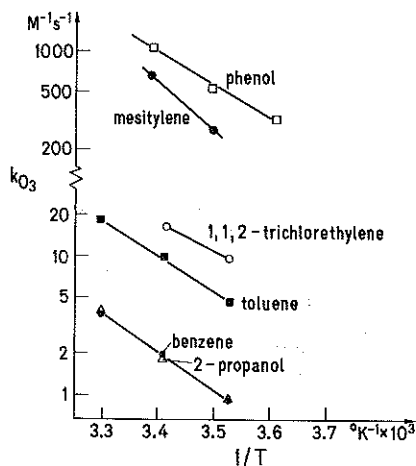
Fig. 6.  $k_{O_3}$  values for selected solutes vs temperature.

Table 4. Reaction-rate constants of miscellaneous compounds\*

Solute	mM	pH	Method <sup>¶</sup>	Scavenger mM		$k_{O_3}$ ( $M^{-1} s^{-1}$ )	(N) <sup>†</sup>
Carbon tetrachloride	5	2	u.v.	—	—	<0.005	(1)
Chloroform	10-40	2	u.v.	—	—	≤0.1	(3)
Bromoform	7	2	I	—	—	≤0.02	(1)
Methylene chloride		2	u.v.	—	—	≤0.1	
Urea	20-130	2/7	u.v.	—	—	~0.05	(8)
<i>n</i> -Propylacetate	130	2	u.v.	<i>t</i> -BuOH	15	0.03 ± 0.01	(1)
Acetone	20-200	2	u.v.	—	—	0.032 ± 0.006	(4)
2-Pentanone	6	2	u.v.	—	—	~0.02	
Malonic acid diethylester	8/70	2	u.v.	—	—	0.06 ± 0.02	(2)
2-Butanone	10-100	2	u.v.	—	—	0.07 ± 0.02	(6)
Saccharose	5-100	2	u.v.	<i>t</i> -BuOH	20-200	0.12 ± 0.02	(7)
Dioxane	6-50	2	u.v.	—	—	0.32 ± 0.03	(7)
Glucose	5-100	2	u.v.	—	—	0.45 ± 0.05	(10)
		6	u.v.	—	—	0.9 ± 0.2	(10)
Diethylether	17-140	2	u.v.	—	—	1.1 ± 0.1	(9)
Dimedone	2.7 · 10 <sup>-3</sup>	2	—	—	—	> 4 · 10 <sup>5</sup>	(2)
Dipropylsulfide	8 · 10 <sup>-3</sup>	2	I	<i>t</i> -BuOH	2	> 2 · 10 <sup>5</sup>	(1)
Ethylmercaptan	8 · 10 <sup>-5</sup>	2	I	<i>t</i> -BuOH	2	> 2 · 10 <sup>5</sup>	(1)

\*For further heterogeneous compounds see Part II.

†See Table 1.

¶See Table 2.

time of ozonation. This indicates that the apparent stoichiometric factor  $\eta$  [cf. equation (1b)] did not vary during ozonation or between series of measurements.

The invariance of  $\eta$  could be due to the fact that the number of ozonation steps which lead to the daughter products  $M_{oxid}$ , does not depend greatly on the ozonation treatments used. This invariance of  $\eta$  facilitates the evaluations of the  $k_{O_3}$  values.

In addition, the fact that  $\eta$  values for different sol-

utes do not vary greatly compared with the wide range of reaction-rate constants, allows one to estimate from the  $k_{O_3}$  values the rate constants  $k_{O_3}/\eta$  which characterize the kinetics of the elimination of the solutes M.

Reaction-rate constants determined from the relative rates of solute elimination correspond only approximately to those determined from the rate of ozone consumption even when these are corrected for

Table 5. Relative reaction-rate constants

(a) Benzene/toluene/methylbenzoate at pH 2 in presence of 10 mg l<sup>-1</sup> propanol as scavenger

Ozone added (mg l <sup>-1</sup> )	$c/c_0$			$k_{II}/k_I$	$k_{rel}$ $k_{III}/k_I$
	I Benzene [0.1]	II Toluene [0.2]	III Methylbenzoate [1.0]		
2	0.62	0.24	(0.86)	3.0	(0.32)
3	0.56	0.13	0.79	3.6	0.40
4	0.49	0.07	0.73	3.7	0.44
5	0.39	0.04	0.66	3.5	0.43
6	0.30	(0.02)	0.60	(3.3)	0.41

(b) Benzene/toluene/ethylbenzene/*n*-alkyl(C<sub>11</sub>-C<sub>13</sub>)benzenesulfonate (Marlon A)

Ozone added (mg l <sup>-1</sup> )	$c/c_0$				$k_{II}/k_I$	$k_{rel}$ $k_{IV}/k_I$	$k_V/k_I$
	I Benzene [2]	II Toluene [1]	IV Ethylbenzene [1]	V Marlon [2.5]			
2	(0.87)	0.60	0.60	(0.89)	(3.7)	(3.7)	—
4	0.68	0.28	0.29	0.75	(3.3)	(3.1)	(0.75)
6	0.59	0.14	0.13	0.62	3.7	3.8	0.90
8	0.42	0.04	0.04	0.46	3.8	3.8	0.92
10	0.29	—	—	0.30	—	—	0.96

[ ] Initial concentrations in mg l<sup>-1</sup>.

individual stoichiometric factors. This is not due to interferences by OH<sup>-</sup> or other free-radical type mechanisms: neither the ratio of the solute concentrations nor further addition of free-radical scavengers had an effect on the  $k_{rel}$  values. However, the difference between absolute  $k_{O_3}$  values and the  $k$  values calculated from  $k_{rel}$  could in some cases be due to some additional transformations of solutes by secondary reactions. Especially the rate of the elimination of aldehydes could be increased by such an additional pathway. Nevertheless, in most cases, results of the relative rates of solute elimination seem still adequate for semi-quantitative verifications of absolute  $k$  values. However, because of the potential inaccuracy of the  $k_{rel}$  values, we base our following discussions only on absolute  $k_{O_3}$  values.

#### Rate constants for substituted benzenes

The reaction-rate constants of different substituted benzenes (see Table 1) vary by many orders of magnitude. They increase in the order expected for reactions with an electrophilic reagent. Data of some representative compounds are plotted in Fig. 7 vs the constant  $\sigma_p^+$  of the Stock-Brown Linear Free Energy Relationship (Exner, 1972). A linear relationship is found. The slope of the line gives a reaction constant  $\rho = -3.1$ . This means that the direct reaction of ozone with the aromatic ring systems is highly electrophilic and highly selective. Corresponding types of correlations were deduced by Wibaut *et al.* (1952) when comparing the rates of ozonation in chloroform with those of nitration, or by Spialter *et al.* (1971), Oulette & Marks (1968), and Whitworth *et al.* (1969) who showed that ozone behaves as an electrophile when hydrosilanes and ring-substituted styrenes are ozonized in organic solvents. That methyl substituents increase the reac-

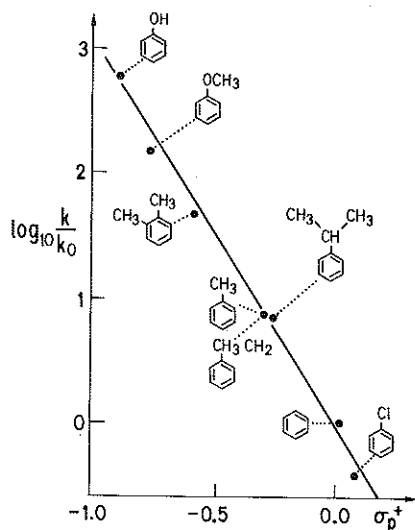


Fig. 7. Stock-Brown plot of  $k_{O_3}$  values of substituted benzenes.  $\sigma_p^+$  values are based on the solvolysis of dimethylphenylcarbonylchloride (Exner, 1972).

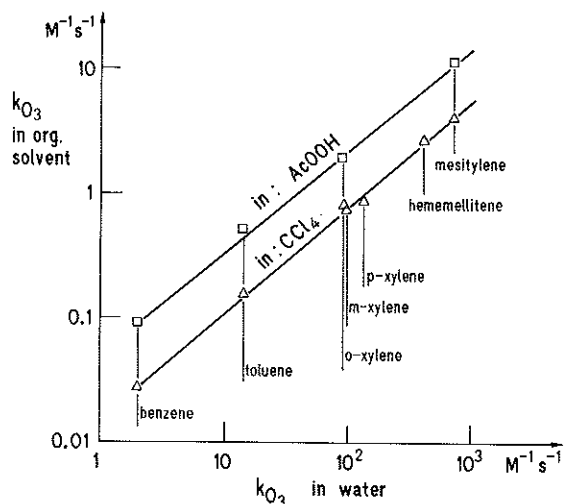


Fig. 8. Comparison of reaction-rate constants determined in different solvents. Values in aqueous sol. at 20°C from this work, in carbon tetrachloride at 20°C and in acetic acid at 25°C from Nakagawa *et al.* (1960).

tivity of the aromatic ring also corresponds with observations made in non-polar solvents and in the gaseous phase (Dijk, 1948; Pate *et al.*, 1976; Sixma *et al.*, 1951; Wibaut *et al.*, 1952).

Extrapolating the results of the Free Energy Relationship to the side of low  $\sigma_p^+$  values leads to the hypothesis that aromatic compounds having a higher delocalisation of electrons will exhibit higher reactivities towards ozone. This is important when ozone is considered for the oxidation of condensed aromatic ring systems such as are often suspect for their cancerogenicity. Furthermore, the experiences that ozone is a highly efficient reagent for eliminating phenolic impurities in water can be explained by the high reaction-rate constants expected for reactions of benzene derivatives of such low  $\sigma_p^+$  values. (For extensive data on phenols see Part II.) On the other side, the observations made in practice that benzene and halogenated or nitrated benzene derivatives are highly inert in ozonation treatments can now also be explained by the high  $\sigma$  values of such compounds.

In carbon tetrachloride the rate constants of reactions of aromatic hydrocarbons are about 100 times lower than in water as is shown by the comparison of data presented in Fig. 8. Because the reaction-rate constants of aliphatic compounds do not show a same solvent effect (see later), the substrate selectivity of ozonations will shift correspondingly with the type of the solvent.

#### Substituted ethylenes

The rate constants for the reactions of a few common substituted ethylenes are listed in Table 2. The values for the hexenols are higher than  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ . However, rate-constants decrease by many orders of magnitude when the hydrogen atoms next to the double bond are replaced by chlorine atoms (see the



Table 6. Comparisons of rate constants of reactions of ozone with olefins and alcohols measured in water with those measured in  $\text{CCl}_4$  (25°C)

	In $\text{H}_2\text{O}$	In $\text{CCl}_4$
$\text{CCl}_2 = \text{CCl}_2$	<0.1	1.0*
$\text{CHCl} = \text{CCl}_2$	17	3.6*
$\text{CH}_2 = \text{CCl}_2$	110	22*
<i>trans</i> $\text{CHCl} = \text{CHCl}$	~5700	591*
<i>t</i> -Butylalcohol	~0.03	0.05†
<i>n</i> -Butylalcohol	0.6	0.39†
Cyclopentanol	2.0	1.35†

\*From Williamson & Cvetanovic (1968).

†From Williamson & Cvetanovic (1970).

series of chloroethylenes) or by carboxylic acid groups (see fumaric and maleic acids).

Similar substituent effects were found by Williamson & Cvetanovic (1968) for a large number of compounds in carbon tetrachloride. They concluded that the decrease in reactivity is due primarily to the inductive effect ( $\text{I}^-$ ) but that steric effects may also play a role.

The rate-constants of reactions of olefinic compounds are about 5 times greater in water than those in carbon tetrachloride (cf. Table 4) although the stoichiometric factor with which ozone reacts with olefinic compounds in water is again 1.0, as previously found in other solvents (Williamson & Cvetanovic, 1968).

#### Substituted alkanes

Alkylamines are well suited for the measurement of the maximal possible rate constant with which ozone in water reacts with an aliphatic alkyl chain; these compounds are soluble in water and at low pH values protonation protects their amino group against ozonation (see Part II). These compounds show very low reaction-rate constants; e.g.  $k \leq 0.02 \text{ M}^{-1} \text{ s}^{-1}$  has been measured for protonated butylamine.

The rate constant for alkyl alcohols are significantly higher and ketones too, except acetone, exhibit significant reaction-rate constants. The  $\beta$ -diketone, dimedone, represents an extreme case. We therefore postulate that  $-\text{CH}_2\text{OH}$  and  $>\text{C}=\text{O}$  groups have an activating effect on the adjacent methylene groups of the aliphatic chain.

The results found for the reactivity of saturated alkyl groups correspond with the low reactivity known for paraffins in non-polar solvents; e.g. for *n*-octane a reaction rate constant of 0.014 has been reported (Williamson & Cvetanovic, 1970).

The rate constants for the alkyl alcohols in water are similar to those measured in carbon tetrachloride by Williamson & Cvetanovic (1970), (see Table 6). The discussion by these authors on the structural effects of alcohols on their reactivities is therefore also applicable to the results found in aqueous solution.

#### Miscellaneous compounds

The carbohydrates investigated also show rather low rate constants (cf. Table 4). Similar observations have been published for their ozonation in non-polar solvents (Horner *et al.*, 1958).

The low  $k$  value of urea shows why urea is highly refractory when its solution (e.g. in swimming pools) is treated with ozone.

The rate constants determined for thio compounds validate the qualitative observations by Mudd *et al.* (1969) that the rates of ozonolyses of thio compounds increase in the order  $k((\text{R}-\text{S})_2) \gg k(\text{R}-\text{SH}) \gg k(\text{RSCH}_3)$ . The high reaction rate constants explain the selectivity with which ozone oxidizes thio compounds to the corresponding sulfoxides when these are present in mixtures of different solutes.

#### Temperature effect

All reaction rate constants tested increase with temperature. For most compounds studied, an Arrhenius plot gives an activation energy of 35–50  $\text{kJ mol}^{-1}$ . These values agree within 8  $\text{kJ mol}^{-1}$  with those measured in carbon tetrachloride or acetic acid (Nakagaya *et al.*, 1960). This effect of temperature on the reaction-rate constants is comparable with that of the hydroxide ion catalyzed decomposition of ozone (Stumm, 1958). Therefore, changes in temperature can hardly shift the amount of ozone decomposition compared to the amount reacting with solutes.

## 6. CONCLUSIONS

#### Methods

Both methods, the measurement of the rate of ozone consumption at varied concentrations of solutes, as well as the measurement of the relative rates with which different solutes are eliminated by ozonation, are suitable to determine rate constants over as wide a range as  $0.1\text{--}10^4 \text{ M}^{-1} \text{ s}^{-1}$ , even when only standard laboratory equipment is used. The main limitation of the measurements is the rate at which ozone decomposes in reactions other than with the specified compound. This decomposition cannot be effectively inhibited by radical scavengers or low pH when reaction times of more than 1000s are considered. Therefore, the solute concentrations used must be high enough so that  $\tau_{\text{O}_3}$  is <1000 s. This condition requires that the ratio of solubility of the solute/rate constant is at least  $10^{-3} \text{ M M}^{-1} \text{ s}^{-1}$ .

The relative reaction-rate method has an additional limitation: because of the wide range of rate constants with which different types of solutes react with ozone, the number of pairs of substances which react with experimental comparable constants (within a factor of about 5) is rather restricted. This method is therefore less widely applicable than it is for the study of reactions which depend less on the type of the solute

structure, e.g. oxidations by OH radicals (Hoigné & Bader, 1976).

#### Ozonation of drinking and wastewater

The result that all direct reactions of dissolved ozone with specified solutes are first order in ozone and in solute concentration, allows one to draw some straightforward conclusion from the rate constants: in many systems the concentration of ozone is kept quite constant during the ozonation time. Under these conditions the half-life of a solute M in a batch-type reactor can be calculated from:

$$t_{1/2} = \frac{0.69}{[O_3] \times k_{O_3}/\eta} \approx \frac{0.69}{10^{-5} \times k}$$

The approximation on the right-hand side is based on the assumption that  $\eta$  is about unity and that the concentration of ozone is of the order of magnitude of  $10^{-5}$  M ( $0.5 \text{ mg l}^{-1}$ ). This is a rather typical value encountered in many waterworks or in studies on disinfections. That means that only those solutes which have a reaction-rate constant of at least  $100 \text{ M}^{-1} \text{ s}^{-1}$  are significantly ozonized during an ozonation process lasting 10 min. The values listed in Tables 1–4 show, that reactions of most solutes have rate constants which are either orders of magnitude above or orders of magnitude below this value. That means that most of the non-dissociating compounds discussed in this Part are either highly reactive or highly inert when classified for practical water treatment ozonation.

However, for the ozonation of solutes which exhibit low reaction-rate constants ( $k \ll 100 \text{ M}^{-1} \text{ s}^{-1}$ ) also oxidations by secondary oxidants which are produced from the decomposition of ozone have to be accounted for. This second pathway is however rather ineffective when the ozonation is performed in the range of very low pH values or in presence of high concentrations of solutes which scavenge OH radicals in competitive reactions (Hoigné & Bader, 1978d, 1979b).

In case of reactive solutes the ratios of reaction-rate constants may well describe the selectivities or sequences with which ozone transforms different types of solutes when these are present in the same solution. Methods to evaluate such selectivities of ozonation reactions have been described by Hoigné & Bader (1978b) and will be summarized by Hoigné (1982).

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