

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

DISSOCIATING ORGANIC COMPOUNDS

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Abstract—Comprehensive lists of rate constants of reactions of ozone with acidic and basic organic chemicals dissolved in water, such as amines, amino acids, carboxylic acids and phenols are reported. The second-order rate constants increase with pH as does the degree of deprotonation of the dissolved substances, e.g. from 1 to 100 M⁻¹ s⁻¹ for formic acid, from 0.2 to 2 M⁻¹ s⁻¹ for glyoxalic acid and from 10³ to 10⁹ M⁻¹ s⁻¹ for phenolic compounds. All results support the conclusions presented in Part I for the electrophilic reactions of ozone with non-dissociating compounds. They are important for the understanding of the pH dependence of the rate and selectivity of ozonation reactions and for explaining the chemical effects of ozone on impurities in drinking water and waste waters.

1. INTRODUCTION

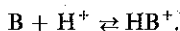
The kinetics of the ozonations of acidic and basic organic compounds, such as phenols and amines or amino acids, dissolved in water are of importance for the understanding of the biological effects of ozone and for the design of water treatment processes. At the pH of biological systems or natural waters the reaction-rates observed for reactions of such solutes are often regulated by the small fraction of deprotonated species present. However, no reaction-rate data for such deprotonated compounds have been published so far except the studies by Taube & Bray (1941) on formic acid and by Hoigné & Bader (1978a, b) on ammonia and by Games & Staubach (1980) on nitrilotriacetate.

Formulation of the kinetic system

Case I (general case). Based on our results presented in Part I (Hoigné & Bader, 1983a) on the kinetics of ozonation reactions, it has been deduced that the observed rate of the reaction of ozone with solutes can best be described by a second order reaction-rate constant, the concentration of ozone and the concentration of the solute reacting with ozone. In cases in which the solutes consist of acids (HB) or bases (B), the rate of the reaction of ozone will however also depend on the degree of dissociation or protonation of these species:



or:



For the latter case the dependence of the rate of disappearance of ozone, $1/\tau_{\text{O}_3}$ can be formulated as:

$$\begin{aligned} 1/\tau_{\text{O}_3} &= - \frac{d[\text{O}_3]}{dt \cdot [\text{O}_3]} = k_{\text{tot}} [\text{B}_{\text{tot}}] \\ &= k_{\text{B}} [\text{B}] + k_{\text{HB}^+} [\text{HB}^+] \\ &= \alpha k_{\text{B}} [\text{B}_{\text{tot}}] + (\alpha - 1) k_{\text{HB}^+} [\text{B}_{\text{tot}}] \end{aligned} \quad (1)$$

where k_{tot} is the apparent reaction-rate constant based on the total concentration of base present, $[\text{B}_{\text{tot}}]$, and k_{B} and k_{HB^+} are individual reaction-rate constants of non-protonated species B and of protonated species HB^+ , respectively. The relative amount of B or HB^+ present in the solution can be calculated from α , the degree of dissociation ($\alpha = [\text{B}]/([\text{B}] + [\text{HB}^+])$). This degree of dissociation can be determined from the pH of the solution and the dissociation constant K of the protonated base:

$$\alpha = 1/(1 + [\text{H}^+]/K_{\text{HB}^+}). \quad (2)$$

Corresponding formulations can be used for the rate law expressions for acids.

Case II. The non-protonized bases (B) [or deprotonized acids (B^-)] often react over a wide pH range many orders of magnitude faster than the protonated compounds HB^+ or HB. Over this region of pH the rate of reaction is determined only by the rate with which B (or B^-) react. That means if:

$$\alpha k_{\text{B}} \gg (1 - \alpha) k_{\text{HB}^+} \quad (3a)$$

Equation (1) reduces to:

$$k_{\text{tot}} = \alpha k_{\text{B}} \quad (3b)$$

When α is expressed by equation (2) and if

$[H^+] \gg K_{HB}$ we may write for (3a):

$$k_{tot} = k_B \cdot K_{HB} / [H^+] \quad (4a)$$

or

$$\log(k_{tot}) = \log k_B + pH - pK_{HB} \quad (4b)$$

Equation (4b) shows that in this case the logarithm of the total reaction-rate constant, k_{tot} , increases linearly with pH, the slope of the line being 1.0.

Corresponding formulations result when an acid HB is considered.

2. EXPERIMENTAL METHOD

Chemicals

See Part I. In addition, butyric acid was purified as its potassium salt by fractional recrystallization from water. Malonic and succinic acids were recrystallized as acids from aqueous solutions. Aniline was vacuum distilled before use. Methylamines were of low purity: tests by gas chromatography showed that the monomethylamine contained 0.1% dimethylamine and 0.5% trimethylamine. The dimethylamine contained 0.5% trimethylamine. Trimethylamine was contaminated by 0.2% methylamine. The absence of interferences from small amounts of impurities present in chemicals were tested by measurements on samples which were pretreated with an amount of ozone expected to oxidize 1–10% of the total solute present.

pH adjustment

See Part I. Only phosphoric acid was used to reach pH values below 2. The pH was determined for all samples before and after ozonation with a glass micro electrode, calibrated with standard buffers between pH 4.0 and 9.0 (Titrisol Merk).

Procedure for determining absolute rate constants

The procedures used are described in Part I (Hoigné & Bader, 1983a) and by Hoigné & Bader (1978a). The kinetics of the systems described in this Part had, however, to be determined as function of pH. The concentration of ionized species was calculated from the total concentration of the solute present, the pH, and the pK. The pK values were from the literature using values at temperatures and ionic strengths comparable to the conditions of our measurements. Further corrections for ionic strength have only been considered for NH_4^+ (Hoigné & Bader, 1978a, b).

Procedure for determining relative rate constants

From the measurements of the relative reaction-rate constants, such as deduced from the relative rate of transformations of pairs of solutes [cf. equation (6), Part I], one series is presented here for exemplification. In this series relative residual concentration of 4-nitrophenol was compared with that of *o*-xylene and mesitylene, when these compounds were ozonated in the same solution. The concentration of *o*-xylene and mesitylene were measured by headspace gas-liquid chromatography (Hoigné & Bader, 1979). The concentration of nitrophenol was determined from its u.v. absorbance at 400 nm after the pH was raised to above 10.

3. EVALUATION OF EXPERIMENTAL DATA AND RESULTS

Absolute second-order reaction-rate constants

The kinetic rules deduced for the ozonation of non-dissociating solutes, described in Part I, can also be used to evaluate the measurements made on aqueous

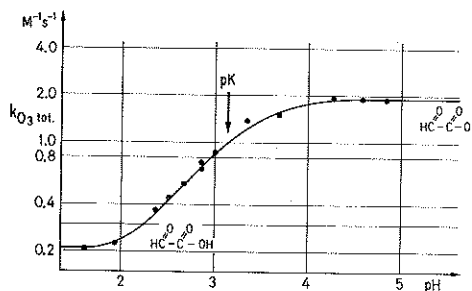


Fig. 1. Rate constant of the reaction of ozone with glyoxylic acid vs pH.

solutions of bases and acids: Over all concentrations used, where the total concentration of solute was much greater than that of ozone, all reactions were first-order with respect to ozone. Therefore, pseudo first-order reaction-rate constants ($1/\tau_{O_3}$ values) could be determined for each solute concentration and pH. From these values second-order reaction constants were deduced.

The second-order reaction-rate constants of the solutes measured in this Part varied from <0.01 to $10^9 M^{-1} s^{-1}$. Because of this wide range of values, different types of data evaluation and presentation had to be adapted: For some series of measurements it was advantageous to calculate second-order rate constants from the $1/\tau_{O_3}$ values by dividing each value by the total concentration of the solute applied. The resulting total rate constants have been tested for different solute concentrations and plotted vs the pH. The reaction-rate constants for the non-dissociated and for the deprotonated species could be deduced from the plateau values which appeared at the pH regions far below and above the pK value of the solutes. Results for glyoxylic acid are given as an example in Fig. 1.

In such cases the reaction-rate constants of the individual species were also determined from linear plots of the total reaction-rate constants vs the degree of dissociation, α . Linear relationships between the reaction-rate constant and α were obtained. Examples are given in Figs 2 and 3. Values extrapolated to

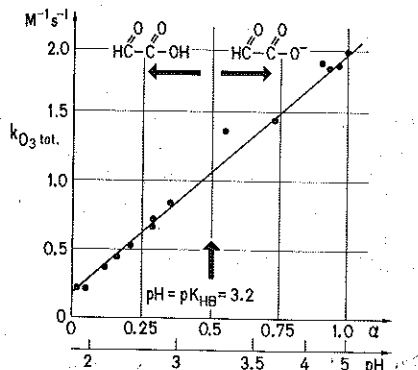


Fig. 2. Rate constant of the reaction of ozone with glyoxylic acid vs degree of deprotonation ($pK_{HB} = 3.2$).

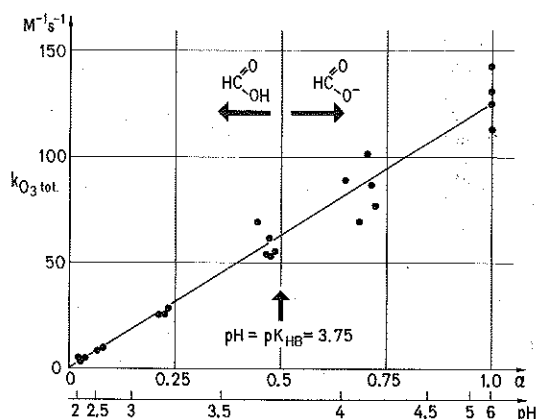


Fig. 3. Rate constant of the reaction of ozone with formic acid vs degree of deprotonation ($pK_{HB} = 3.75$).

$\alpha = 0$ or to $\alpha = 1.0$ give the rate-constants for the non-dissociated acid (HB) or of the anionic species (B^-).

In other cases, such as for phenolic compounds, the upper plateau value is too high to be measured by our methods. In these cases the total rate constants increased over a wide range of pH values, after the lower plateau was left, by a factor of 10 per pH, i.e. there the increment of rate corresponds with the degree of dissociation of the solute [cf. equations (4a) and (4b) and Fig. 4]. For presenting the results, the total rate constants were plotted vs pH using a log-scale. Reaction-rate constants of the dissociated species were deduced from these apparent total reaction-rate constants by accounting for the degree of dissociation. The assumptions were tested by the consistency of all data determined for the pH-region above the plateau value.

In other cases, where the protonized species do not contribute to the overall rate of reaction such as in case of formic acid or amines or amino acids, a direct determination of an average rate constant deduced from all measurements performed on a solute at different pH values was more appropriate. In these cases

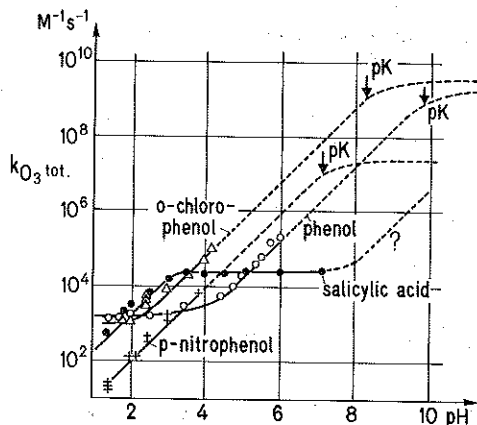


Fig. 4. Rate constants of reactions of ozone with phenolic compounds vs pH. (---) Extrapolated (assuming slope = 1 for the linear portions).

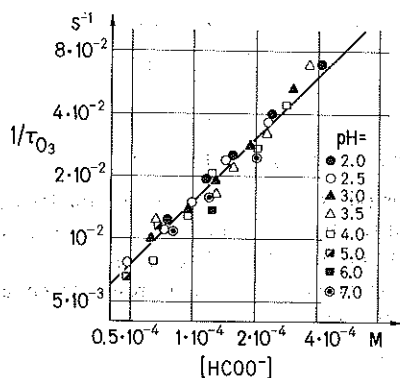


Fig. 5. Rate of ozone consumption ($1/\tau_{O_3}$) vs the formate ion conc. in the presence of different amounts of formic acid. Calculated concentrations of $HCOO^-$ are based on pK_{HB} (formic acid) = 3.75.

the $1/\tau_{O_3}$ values were plotted vs the calculated concentration of the reacting base. The method is that described in Part I for non-dissociating compounds, except that the concentrations of the reacting species were varied by using different solute concentrations and different pH values. Figures 5, 6 and 7 give examples. Straight lines of slope 1.0 were visually fitted to the central part of the series of measurements;

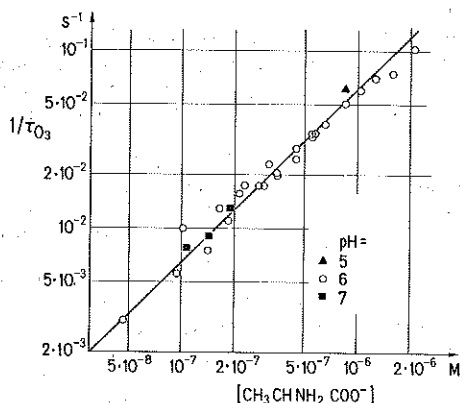


Fig. 6. Rate of ozone consumption vs the conc. of deprotonated α -alanine in the presence of different total amounts of α -alanine. Calculated conc. of the deprotonated amine is based on pK_{HB^+} ($CH_3CHNH_3^+COO^-$) = 10.0

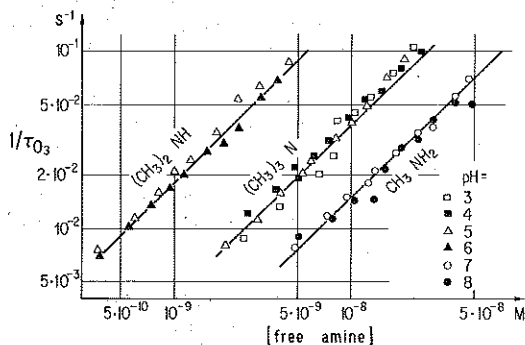


Fig. 7. Rate of ozone consumption vs the conc. of free methyl amines in the presence of different total amounts of amines. Calculated conc. of the free amines are based on $pK_{HB^+} = 10.7$ for $CH_3NH_3^+$; 11.0 for $(CH_3)_2NH_2^+$ and 9.9 for $(CH_3)_3NH^+$.

i.e. it was assumed that the $1/\tau_{O_3}$ values only depended on the concentration of the deprotonated species (B^- in case of acids, or B in case of amines or amino groups of amino acids). The second-order reaction-rate constant was calculated by dividing the mean $1/\tau_{O_3}$ by its corresponding concentration as determined from the graph.

The resulting numerical values of the second-order reaction-rate constants are given in Tables 1–3. Whenever possible the individual constants deduced for the anionic and non-ionic species are included.

Carboxylic acids

The results given in Table 1 show that the reaction-rate constants of aliphatic carboxylic acids are rather low when the compounds do not contain other chemical groups which may react. Acetic and oxalic acids and their anions react so slowly that even for high solute concentrations no reaction rate could be determined. In contrast, the rate constant for the reaction of the formate ion is rather high ($140 \text{ M}^{-1} \text{ s}^{-1}$). But a plot of the total rate constant observed for this compound vs the degree of dissociation α gives for $\alpha = 0$, that means for non-dissociated formic acid, a rate constant which is not significantly different from zero (see Fig. 3). In correspondence, the total rate of reaction of the formic acid/formate ion system is independent of the concentration of the non-dissociated species, even when the total rate is determined at pH 2.0, where 98% of the total acid is not dissociated (see Fig. 5).

Carboxylic substituents decrease the rates with which adjacent aryl or alkene groups react with ozone. For instance the reaction-rate constants of undissociated benzoic acid and salicylic acid are lower than those of benzene and phenol. Also maleic acid and fumaric acid show relatively low rate constants compared to those of other olefinic compounds. In contrast, deprotonized carboxyl substituents (pH > 3) may give some enhancement for the reactions of the adjacent groups. This becomes apparent in the case of maleic acid or aryl compounds as represented by the salicylate ion; in case of salicylic acid the log of the rate constant increases with pH up to pH = 3 what corresponds to the pK_a value of the acid (see Table 1 and Fig. 4).

Phenolic compounds

The rate constants of phenol and substituted phenols and of their dissociated species, the phenolate ions, are listed in Table 2. In addition, Fig. 4 illustrates examples of the pH dependency of the total rate constants.

All the phenols tested, except nitrophenol and non-dissociate salicylic acid (< pH 3) have high reaction-rate constants. These increase additionally by several orders of magnitude when the phenolic group dissociates. The rate constants of some substituted phenolate ions even approach values expected for diffusion controlled reactions.

Therefore the total reaction-rate constants of these compounds increase over a wide range of pH values by a factor of 10 per pH unit, what is in direct correspondence with the increment of the degree of dissociation. A plateau-value for non-dissociated phenol can be observed only at rather low pH values where less than 10^{-5} parts of the phenolic groups are dissociated. The salicylate ion is an exception; for this compound the plateau value extends to pH = 7. This corresponds to the very low dissociation constant of the phenolic group of the salicylate ion.

The reactivity of polychlorinated phenols or of nitrophenol is lower than that of phenol. However, these more acidic phenols have pK_{HB} values which are a few units below that of phenol. Therefore, at similar pH values their degree of dissociation is a few orders of magnitude larger than that of phenol. The apparent total rate of reaction in the range of pH 3 to pH < pK_{HB} therefore becomes of comparable magnitude to that of phenol.

In contrast, the aromatic ring of the salicylate ion seems to be somewhat activated for reactions with ozone by the carboxylate group. This group is highly dissociated above pH = 3 ($pK = 3.0$). However, the phenolic group of the salicylate ion is a very weak acid ($pK_2 = 13$) and the effect of its dissociation on the reaction rate constant does not become significant even at pH 6 (there still only 10^{-7} parts of this phenolic compound are dissociated). At this pH the salicylic acid/salicylate ion system therefore has a lower total reaction-rate constant than the phenol/phenolate system.

Ammonia, amines and amino acids

The selection of amino compounds studied was made on the basis that the amino group was expected to be the only site for reaction with ozone. Results for the different types of compounds are presented in Figs 6 and 7 and in Table 3.

We concluded from a preliminary study that protonated amino groups do not react with ozone, i.e. the rate of reactions of these compounds is determined only by the concentration of free amino groups, provided that there are present no other substituents which react [cf. equation (4a)]. This assumption was tested for each series of measurements by including samples at pH values as low as 2 where the degree of dissociation of the protonated amino groups is very low. Ammonia, methylamines, butylamine and most of the amino acids did not react under these conditions. The result for butylamine also shows that *n*-alkyl groups do not react with ozone when substituted with protonated amines. Therefore we assume that *n*-alkyl residues will not react with ozone provided that no other substituents exert an activating effect (cf. Part I).

When measured above pH 4 the pseudo-first order reaction-rate constant of ozone, $1/\tau_{O_3}$, always increased only with the concentration of the free amine present in the solution. Examples are given in Figs 6

Table 1. Reaction-rate constants of carboxylic acids (HB) and ions (B⁻)

Solute	pK _{HB}	mM	pH range	Method*	Scavenger	k _{meas} (M ⁻¹ s ⁻¹)	k _{HB†} (M ⁻¹ s ⁻¹)	k _{B‡} (M ⁻¹ s ⁻¹)	(N)†	calc. k _{tot} for pH = 8 (M ⁻¹ s ⁻¹)
Acetic acid	4.75	1000	2.5/5	u.v.	—	≤ 3 · 10 ⁻⁵	≤ 3 · 10 ⁻⁵	≤ 3 · 10 ⁻⁵	(4)	≤ 3 · 10 ⁻⁵
Propionic acid	4.9	1000	2/5	u.v.	—	< 4 · 10 ⁻⁴	1 ± 0.5 · 10 ⁻³	2 ± 1 · 10 ⁻³	(4)	2 ± 1 · 10 ⁻³
Butyric acid	4.8	50	2/4	u.v.	—	≤ 6 · 10 ⁻³	≤ 6 · 10 ⁻³	≤ 4 · 10 ⁻²	(8)	≤ 4 · 10 ⁻²
Oxalic acid	1.2/4.2	100-500	5-6	u.v.	—	< 8 · 10 ⁻³	< 8 · 10 ⁻³	≤ 4 · 10 ⁻²	(9)	≤ 4 · 10 ⁻²
Glutaric acid	4.3/5.4	200-600	4/6	u.v.	—	< 3	(8 ± 2) · 10 ⁻³	(8 ± 2) · 10 ⁻³	(2)	(8 ± 2) · 10 ⁻³
Succinic acid	4.2/5.6	100-700	4-6	u.v.	—	< 4	(3 ± 1) · 10 ⁻²	(3 ± 1) · 10 ⁻²	(7)	(3 ± 1) · 10 ⁻²
Glyoxylic acid	3.2	1-15	1.5-5	u.v.	t-BuOH	0.17 ± 0.4	1.9 ± 0.2	1.9 ± 0.2	(14)	1.9 ± 0.2
Malonic acid	2.8/5.7	2-20	2	u.v.	—	< 4	7 ± 2	7 ± 2	(11)	7 ± 2
Formic acid	3.75	1-20	2-4	u.v.	PrOH	5 ± 5	100 ± 20	100 ± 20	(25)	100 ± 20
Maleic acid	1.8/6.1	10-70	2	u.v.	t-BuOH	1 · 10 ³	5 ± 5	> 5 · 10 ³	(13)	> 5 · 10 ³
Salicylic acid	3§	(0.03-1) · 10 ⁻²	1.5-7	I	t-BuOH	5 · 10 ³	< 500	(2.8 ± 3) · 10 ³	(13)	< 5 · 10 ⁴
Fumaric acid	3.0/4.4	10-100	2	I	t-BuOH	6 · 10 ³				> 10 ⁵
			5	I		1 · 10 ⁵				

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

†Number of measured rate curves [O₃]_t vs time.

‡Values from measurements of k vs pH.

§pK of acid. The phenolate ion does not contribute to k_{tot} below pH = 7 (cf. Fig. 4 and Table 2).

Table 2. Reaction-rate constants of phenols (HB) and phenolate ions (B⁻)[†]

Solute	pK _{HB}	mM	pH range	Scavenger	mM	k _{HB} ⁻ (M ⁻¹ s ⁻¹)	k _{B⁻} (M ⁻¹ s ⁻¹)	(N) ^{††}	calc. k _{tot} for pH = 8 (M ⁻¹ s ⁻¹)
Phenol	9.9	(0.4-4) 10 ⁻²	2-6	<i>t</i> -BuOH	3	1.3 ± 0.2 · 10 ³	1.4 ± 0.4 · 10 ⁹	(17)	18 · 10 ⁶
2-Chlorophenol	8.3	0.004-1	1.8-4	<i>t</i> -BuOH	3	1.1 ± 0.3 · 10 ³	0.2 ± 0.1 · 10 ⁹	(16)	66 · 10 ⁶
4-Chlorophenol	9.2	0.002-1	1.5-6	<i>t</i> -BuOH	3	600 ± 100	0.6 ± 0.2 · 10 ⁹	(30)	34 · 10 ⁶
2,3-Dichlorophenol	7.7	0.03-0.3	2	<i>t</i> -BuOH	3	< 2 · 10 ³		(6)	
2,4-Dichlorophenol	7.8**	0.03-0.3	1.5-3	<i>t</i> -BuOH	3	< 1.5 · 10 ³	~ 8 ± 4 · 10 ⁹	(9)	~ 5 · 10 ⁹
2,4,6-Trichlorophenol	6.1**	0.2-0.3	1.3-1.5	<i>t</i> -BuOH	3	< 10 · 10 ³	> 0.1 · 10 ⁹	(4)	> 10 ⁹
2,4,5-Trichlorophenol	6.9**	0.2-0.3	1.2-1.5	<i>t</i> -BuOH	3	< 3 · 10 ³	> 1 · 10 ⁹	(2)	> 10 ⁹
penta Chlorophenol	4.7**	0.3	2	AcOH	3		≥ 300 · 10 ³	(1)	≥ 10 ⁵
4-Nitrophenol	7.2	0.01-1.4	1.5-3.0	<i>t</i> -BuOH	2-7	< 50	16 ± 5 · 10 ⁶	(20)	14 · 10 ⁶
2-Cresol	10.2	0.01-0.1	1.5/2.0	<i>t</i> -BuOH	7	12 ± 3 · 10 ³		(6)	
3-Cresol	10.0	4 · 10 ⁻³	1.5/2.0	<i>t</i> -BuOH	7	13 ± 3 · 10 ³		(2)	
4-Cresol	10.2	0.01	1.5/2.0	<i>t</i> -BuOH	7	30 ± 6 · 10 ³		(2)	
Salicylate ion	13.4 ^{†††}	(0.03-1) 10 ⁻²	3-7	<i>t</i> -BuOH	4	30 ± 10 · 10 ³		(13)	< 300 · 10 ³
Salicylic acid	3.0/13.4 ^{†††}	0.1-1 · 10 ²	1.2	<i>t</i> -BuOH	4	< 500		(1)	≥ 300 · 10 ³
Resorcinol	9.8	0.003	2	<i>t</i> -BuOH	4		≥ 300 · 10 ³	(1)	≥ 300 · 10 ³

[†]See Table 1.^{††}All measurements by the indigo method.^{†††}pK_{HB} of phenolic group.^{**}pK_{HB} values from own measurements performed with same buffers and pH calibrations as those used for kinetic experiments. Method: The conc. of B⁻/HB was measured by u.v. absorption vs pH (multicomponent method).

Table 3. Reaction-rate constants of amino and other nitrogenous compounds and thiocompounds

Solute	pK _{HB+}	mM	pH range	Method*	Scavenger	mM	k _{meas.} (M ⁻¹ s ⁻¹)	k _{HB+} † (M ⁻¹ s ⁻¹)	k _{B+} ‡ (M ⁻¹ s ⁻¹)	(N)†	calc. k _{tot} for pH = 8 (M ⁻¹ s ⁻¹)
Ammonia	9.3	3-22	2/7-8	u.v.	NaCHO ₃	20		0.0	20 ± 2	(20)	~1.0
Methylamine	10.7	0.02-2	7-8	u.v.	NaCHO ₃	20			<140 ± 30 · 10 ³	(20)	<280
Dimethylamine	11.0	0.04-4	5-6	u.v.	—	—	0.13 ± 0.2	<0.13 ± 0.2	19 ± 4 · 10 ⁶	(30)	~20 · 10 ³
Trimethylamine	9.9	2-200	3-5	I	PrOH	1			4.1 ± 0.8 · 10 ⁶	(7)	~50 · 10 ³
Propylamine		200/400	2	u.v.	—	—	≤0.01	≤0.01		(2)	
Butylamine	10.7	0.1-10	6-7	u.v.	NaHCO ₃	20			170 ± 0.05 · 10 ³	(20)	~340
Aniline	4.6	2-15 · 10 ⁻³	1.2/2	u.v.	—	—	≤0.02	≤0.02		(1)	
Glycine	9.9	0.03-3	6/7	u.v.	t-BuOH	10			90 ± 20 · 10 ⁶	(5)	~10 ⁸
		600	2	u.v.	—	—	~50 · 10 ⁻³		130 ± 20 · 10 ³	(20)	1.6 · 10 ³
α-Alanine	10.0	0.1-80	5/7	u.v.	—	—	~3 · 10 ⁻³		64 ± 12 · 10 ³	(17)	640
		600	2	u.v.	—	—			62 ± 12 · 10 ³	(2)	
β-Alanine	10.3	4-160	5/6	u.v.	t-BuOH	10				(11)	310
Cystein		0.003-0.03	2	I	t-BuOH	10	30 ± 10 · 10 ³			(4)	
Cysteine		0.08-0.04	1.8	I	t-BuOH	10	550 ± 10			(5)	
		0.02-0.2	3.1	I	t-BuOH	10	1 ± 0.2 · 10 ³			(5)	
Methionine		3 · 10 ⁻³	2.0	I	t-BuOH	10	>500 · 10 ³			(1)	
Creatine		50	2	I	t-BuOH	10	~0.5			(1)	
Creatinine		50	6	I	t-BuOH	10	~2			(1)	~2
		7	2	I	t-BuOH	40	~2			(1)	~2
Imidazole	7.1	0.007-0.7	2-6	I	—	—	23-150 · 10 ³	22 ± 5	400 · 10 ³	(13)	~360 · 10 ³
Pyridine	5.2	30	3-7	I	t-BuOH	70	0.05-3	0.01 ± 0.01	3 ± 0.5	(5)	~3
Nitrosodimethylamine		4	5	I	t-BuOH	1/60	~10			(2)	~10
Urea		20-130	2/7	u.v.	—	—	~0.05			(8)	~0.05

*††See Table 1.

and 7. In these log-log scale presentations the lines are drawn with a slope of 1.0 in order to facilitate the testing of the assumption that the rate of reaction was first order with respect to the concentration of the free amino groups over all the pH ranges and concentrations of total amino compounds used for measurements.

The rate constant for free ammonia reacting with ozone is about $20 \text{ M}^{-1} \text{ s}^{-1}$. When the ammonia hydrogen atoms are replaced by methyl groups, the rate of reaction increases by many orders of magnitude. The rate constant for dimethylamine is 10^6 times greater (for monomethylamine only the upper limit for the rate constant can be given because of the presence of dimethylamine as an impurity). Also alkyl groups such as present in butylamine give high activations of the amino groups and the amino acids glycine and alanine show comparable high reaction-rate constants when not measured at very low pH values.

Extremely high rates of reaction were found for the amino acids which contain thio groups (cystine, cysteine, methionine). It must however be assumed that in these cases the thio compounds themselves are the centers which determine the reaction rate.

Organometallic compounds

Tin-organic cations reacted so slowly that no exact reaction-rate values could be measured. The rate constants determined are approximately: Me_3SnCl (pH 3.3) $0.0006 \text{ M}^{-1} \text{ s}^{-1}$; Bu_3SnCl (pH 2.3–4) 1.7; Bu_2SnCl_2 (pH 1.9) 1.5. No reaction of methylmercury cation, methylmercury chloride or methylmercury hydroxide could be measured ($k < 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). Such solutes even stabilized the ozone by quenching a radical-type auto-catalytic reaction which otherwise accelerates the decomposition of ozone in water (for details see Hoigné & Bader, 1978b).

Determination of relative reaction-rate constants

An example of results of measurements of relative rate constants with which competing solutes in a solution are transformed by ozone as a function of pH is presented in Fig. 8. There the rate of reaction of

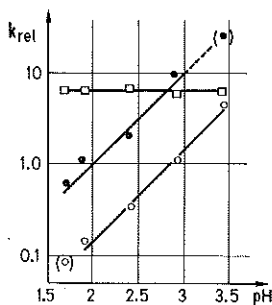


Fig. 8. Relative reaction-rate constants for solute elimination as functions of pH. \square mesitylene/*o*-xylene; \bullet 4-nitrophenol/*o*-xylene; \circ 4-nitrophenol/mesitylene. Initial concentrations: mesitylene—0.02 mM; *o*-xylene—0.01 mM; 4-nitrophenol—0.04 mM; ozone—0.04–2 mM.

4-nitrophenol relative to *o*-xylene and mesitylene (1,3,5-trimethylbenzene) is compared: The rate constant for the reaction of *o*-xylene relative to mesitylene is about 6 and is independent of pH. This k_{rel} found for this reference pair is in fair agreement with that calculated from the ratio of the pH invariant constants with which ozone reacts with these two solutes ($k_{\text{rel, calc.}} = 8$, see Part I, Table 1). This test shows that OH^\cdot radicals do not significantly affect the system; these radicals would eliminate the two solutes with a k_{rel} of only about 1.0 (Hoigné & Bader, 1976). In contrast to the values of this test pair, the k_{rel} values of 4-nitrophenol/*o*-xylene and 4-nitrophenol/mesitylene increase by a factor of 10 per pH increment. This now indicates that the k_{rel} values of 4-nitrophenol to *o*-xylene and mesitylene increase with the degree of dissociation of the phenolic group. These k_{rel} values of the elimination of these solutes agree well with those calculated from the ratio of the individual second-order rate constants, k_{O_3} , which were determined from the rate of ozone depletion.

4. DISCUSSION AND CONCLUSIONS

The rates with which many of the organic bases or acids react with ozone increase considerably with the degree of dissociation of their protonated species. This increment can achieve a factor of 10 per pH over a wide range of pH values, when these are below the $\text{p}K_{\text{HB}}$ value of the solute. In some cases (carboxylic acids and phenols), such an activation by deprotonation is probably due to the enhancement of the nucleophilicity of the site of reaction by an inductive or mesomeric effect. In other cases (amino compounds) the activation can be explained by assuming that the reacting group reacts only with ozone when not protonated.

In order to facilitate comparisons of phenomenological observations of product formations described by many authors with reaction-rate constants, Tables 1–3 also include the total reaction-rate constants extrapolated for pH 8. This pH was chosen for reference because this is common for many types of natural waters used for drinking water and also for other aqueous solutions of interest in connection with effects of ozone on microbiological systems.

The data in Table 1 explain why formate, malonate and glyoxylate are so often observed as significant intermediates when organic compounds are ozonated (Casalini *et al.*, 1977; Gilbert, 1978, 1979; Mallevalle, 1980; Joy *et al.*, 1980; Struit *et al.*, 1977). They also indicate why these intermediates are only slowly further oxidized when the time of ozonation is extended and why the oxidations are faster when the pH is above 3.

In addition, the low reaction-rate constants determined for acetic and oxalic acids and their anions allow clear explanations of the many observations that such compounds always accumulate as final products

when any type of reactive organic aqueous solutes is ozonized in water (cf. Gilbert, 1974, 1978; Gould & Weber, 1976; Mallevalle, 1980; Mofizud-Din Ahmed & Kinney, 1950; Singer & Gurol, 1983; Struit *et al.*, 1978).

A further corollary of these data for carboxylic acids is that the overall oxidation of organic material to CO₂ will be delayed whenever the oxidations lead to oxalic or acetic acid as intermediates. However, in cases where the oxidations form formate ions, mineralization to CO₂ will be less delayed. Therefore the occurrence of a full mineralization of organic solutes will largely depend on whether formate ions or oxalate and acetate ions are formed as intermediate products.

The high reaction-rate constants given in Table 2 for phenols at pH 8 explain the practical experiences that these compounds can be easily transformed by ozone when present in drinking- or wastewater (for such experience see Casalini, 1977; Caprio *et al.*, 1979; Doré *et al.*, 1978a, b; Eisenhauer, 1968; Gould & Weber, 1976; Singer & Gurol, 1983; Yamamoto *et al.*, 1979). For most types of technical ozonation processes, the rates of the reactions are expected to be so high that the overall rate of transformation will be limited by the rates of mass-transfer and mixing processes (Singer & Gurol, 1983 and lit. cited therein; Hoigné, 1978). Furthermore, it is probably valid to assume that the concentrations of ring-hydroxylated products cannot reach any significant values even if these compounds are produced with a high yield as intermediate oxidation products from the reaction of ozone (or OH[•] radicals) with any type of substituted benzenes. Whenever such compounds are observed as intermediates it must be concluded that ozone had decomposed so fast that ozone was ineffective and that most oxidations were only due to the reactions of OH[•] radicals (Hoigné, 1978).

The high rate constants for reactions of amines or thio compounds (see Table 3) are of interest in connection with the high sensitivity of biological systems towards ozone. Because thio compounds are often the cause of smell of exhaust gases, these data are also of relevance when ozone is used to deodorize industrial wastewaters or gaswashing solutions (Neytzell-De Wilde, 1977). From the data in Table 3 it is also clear why ammonia present in water is refractory. In addition the data explain why ammonia will consume ozone only slowly even when it is present at rather high concentrations (Hoigné & Bader, 1978a, b).

It should, however, be kept in mind that the compounds of low reactivity, such as carboxylic acids, may be oxidized by secondary oxidants (e.g. OH[•] radicals) produced by a preliminary decomposition of aqueous ozone. The yields of such reactions will not only depend on the amount of decomposed ozone but also on the total amount of aqueous solutes which scavenge these non-selective oxidants in concurrent reactions (Hoigné & Bader, 1976, 1979). The quantitative interrelations of the two reaction mechanisms,

the direct reactions of ozone and OH[•]-type radical reactions, will be described in a forthcoming review (Hoigné, 1982).

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