PERKIN 2

Determination of fast ozone reactions in aqueous solution by competition kinetics

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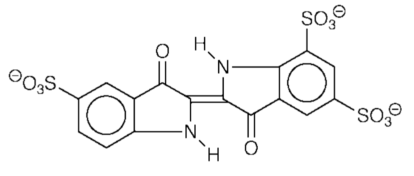
High ozone rate constants (in water) cannot be determined directly by stopped-flow techniques. Competition experiments with buten-3-ol ($k = 7.9 \times 10^4$ dm^3 mol^{-1} s^{-1}; Dowideit and von Sonntag, *Environ. Sci. Technol.*, 1998, **32**, 1112), based on reasonably long-lived intermediates, have been set up with 1,4-dimethoxybenzene (DMB; intermediate at 250 nm measured at 3 s) and 1,3,5-trimethoxybenzene (TMB; intermediate at 260 nm, measured at 10 s). They yielded k(O$_3$ + DMB) = 1.3×10^5 and k(O$_3$ + TMB) = 9.4×10^5 dm^3 mol^{-1} s^{-1}, respectively. A competition of 1,3,5-trimethoxybenzene with indigotrisulfonate, monitored by the bleaching of the indigo derivative at 600 nm, yielded a rate constant of 9.4×10^7 dm^3 mol^{-1} s^{-1} for this compound. This convenient and highly reactive competitor now allows us to determine other very high ozone rate constants. As an example, its reaction with DABCO ($k = 1.7 \times 10^6$ dm^3 mol^{-1} s^{-1}) has been determined. Its direct reaction with ozone (by following the decay of the absorption at 260 nm) can only be determined in a pH range where DABCO is still largely protonated [k(O$_3$ + DABCO/H$_2$$^{2+}$) < 30 dm^3 mol^{-1} s^{-1}; k(O$_3$ + DABCO/H$^+$) = 3.5×10^3 dm^3 mol^{-1} s^{-1}], and the rate constant of the fully deprotonated amine can only be arrived at by extrapolation [k(O$_3$ + DABCO) = 3.2×10^6 dm^3 mol^{-1} s^{-1}].

Ozonation is gaining importance in drinking- and waste-water processing. This requires a better knowledge of both the products and the rate of reaction of pollutants to be degraded by ozone. Ozone rate constants of some 200 compounds have been determined and are tabulated.[1] With compounds that do not absorb in the wavelength region of ozone absorption (λ_{max} = 260 nm) and react only slowly with ozone the decay of the ozone absorption can be followed spectrophotometrically. If the substrate is in large excess, *i.e.* when the kinetics of ozone consumption follow pseudo-first-order kinetics, the choice of the absorption coefficient [*e.g.* ε(260 nm) = 2900 dm^3 mol^{-1} s^{-1},[2] 3150 dm^3 mol^{-1} s^{-1},[3] 3314 dm^3 mol^{-1} s^{-1},[4]] is of no importance. The range of rate constants that can be measured directly in this way can be extended with the help of the stopped-flow technique. Lowering the substrate concentration, *i.e.* shifting the reaction conditions towards second-order kinetics, allows us to measure even higher rate constants. However, this method is fraught not only with greater uncertainties (*e.g.* it requires an exact knowledge of the ozone concentration; note the variation in the reported absorption coefficients) but also with a lower sensitivity due to the lower ozone concentrations that have to be used under these conditions. It also suffers from the possibility that products of the ozone-induced reaction may speed up the ozone decomposition, *e.g.* by an OH-radical-induced chain reaction or by the formation of products which react much more rapidly with ozone.

When the substrate itself absorbs strongly in the UV, *e.g.* aromatic compounds, the kinetics of ozone reactions can no longer be followed under the conditions of pseudo-first-order kinetics, *i.e.* with a large excess of the substrate. In such a case, ozone consumption can be followed, as a function of the reaction time, by titrating the remaining ozone concentration with an ozone scavenger which is very rapidly bleached. For this purpose, potassium indigotrisulfonate [ε(600 nm) ≈ 20000 dm^3 mol^{-1} cm^{-1},[5] the technical product has a stated purity of 85%] is commonly used.[5–7] It is bleached with a rate constant > 10^7 dm^3 mol^{-1} s^{-1}.[7] In a stopped-flow experiment (using a delay line) this approach can also be used and thus allows the determination of otherwise inaccessible higher rate constants.



Indigotrisulfonate

Amines and phenolates react much more rapidly with ozone than their corresponding acids. Because of the high reactivity of the former, rate constants have to be determined in a pH range where their acid forms predominate, and based on their pK_a values the rate constants of their basic forms are then obtained by extrapolation.[8–10]

Yet, there are many highly reactive compounds, *e.g.* indigotrisulfonate, whose rate constants with ozone are too high and thus cannot be determined by this approach. In the present paper it will be shown that this may be done by competition kinetics.

Experimental

Potassium indigotrisulfonate (Riedel-de Haën), 1,4-dimethoxybenzene, 1,3,5-trimethoxybenzene (Fluka), TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl; Aldrich) and DABCO (1,4-diazabicyclo[2.2.2]octane; Aldrich) were used without further purification. According to our ozonation experiments, the indigotrisulfonate is approx. 85% (see also ref. 6), and the calculated rate constant is based on this value. Solutions were made up in Milli-Q (Millipore) filtered water. Ozone was generated using an oxygen-fed ozonator (SWO-70, WEDECO). The stopped-flow setup (SFM-3, Biologic) was equipped with a diode array detector (Tidas 16 J&M, Aalen). Formaldehyde has been determined by the Hantzsch method[11] or, when coloured material is formed, *e.g.* in the ozonation of halogenated pheno-

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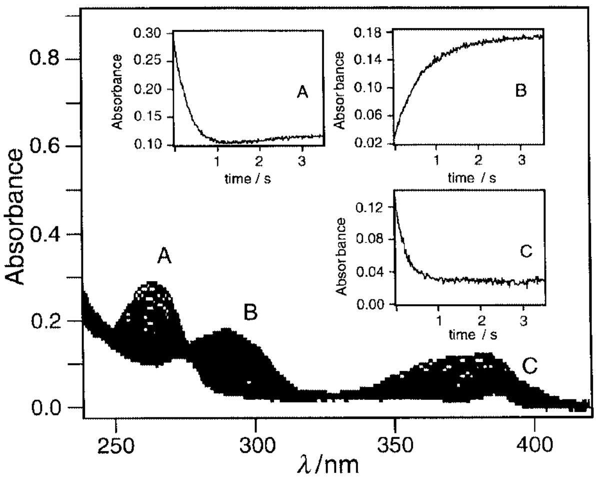

Fig. 1 Formation and decay of intermediates in the reaction of ozone with 1,3,5-trimethoxybenzene. Insets A–C: kinetics at 260, 290, and 360 nm, respectively.

lates, by HPLC of the corresponding 2,4-dinitrophenylhydrazone.[12]

Results and discussion

In competition kinetics, two substrates (here R_1 and R_2) react with the reagent (here ozone). While the product of one of the reactions can be monitored [*e.g.* by the formation (build-up of an absorption) of a product, *e.g.* P_1, or the destruction (bleaching) of one of the components, *e.g.* R_1 [reaction (1)], the other reaction [reaction (2)] remains silent.

$$R_1 + O_3 \longrightarrow P_1 \qquad (1)$$

$$R_2 + O_3 \longrightarrow P_2 \qquad (2)$$

At a given initial ozone concentration ($[O_3] \ll [R_1]$ and $[R_2]$), relationship (3) holds ($[P_1]_o$ is the concentration of the

$$\frac{[P_1]}{[P_1]_o} = \frac{k_1[R_1]}{k_1[R_1] + k_2[R_2]} \qquad (3)$$

measured product in the absence and $[P_1]$ in the presence of the other competing substance, R_2) which can be reorganized yielding eqn. (4).

$$\frac{[P_1]_o}{[P_1]} = \frac{k_1[R_1] + k_2[R_2]}{k_1[R_1]} = 1 + \frac{k_2[R_2]}{k_1[R_1]} \qquad (4)$$

Plotting $([P_1]_o/[P_1]) - 1$ *vs.* $[R_2]/[R_1]$ yields a straight line with a slope of k_2/k_1. Since one of the rate constants is known, the other can be calculated.

In practice, it is convenient to have competitors at hand whose rate constants are not too different (*i.e.* by not more than two orders of magnitude). For setting up such a series of competing reactions, we have been aided by the observation that the reaction of 1,4-dimethoxybenzene and 1,3,5-trimethoxybenzene with ozone yields sufficiently long-lived intermediates to monitor their reactions with ozone. In the case of the reaction of ozone with 1,3,5-trimethoxybenzene, very complex kinetics of the formation and decay of various intermediates are observed (Fig. 1), and they do not allow us to extract the rate constant of 1,3,5-trimethoxybenzene with ozone. It can be seen, however, that the rise at 290 nm (Fig. 1, inset B; at this wavelength the educt has only an absorption coefficient of $\varepsilon = 70$ dm^3 mol^{-1} cm^{-1}) reaches a plateau at about 3 s, and this change in absorption, which is proportional to the ozone concentration (in the presence of an excess of 1,3,5-trimethoxybenzene), can be used for monitoring the reaction of ozone with this compound.

Table 1 Compilation of ozone rate constants pertinent to this study

Compound	Rate constant/ dm^3 mol^{-1} s^{-1}	Reference
Buten-3-ol	7.9×10^4	13
1,4-Dimethoxybenzene	1.3×10^5	This work
1,3,5-Trimethoxybenzene	9.4×10^5	This work
DABCO/H$_2^{2+}$	<30	This work
DABCO/H$^+$	3.5×10^3	This work
DABCO (by extrapolation to high pH)	3.2×10^6	This work
DABCO (by competition)	1.7×10^6	This work
Pentachlorophenolate	1.2×10^6	14
Pentabromophenolate	1.7×10^6	14
2,4,6-Triiodophenolate	6.8×10^6	14
TEMPO	1.3×10^7	15
Indigotrisulfonate[a]	9.4×10^7	This work

[a] Taking its purity as 85%.

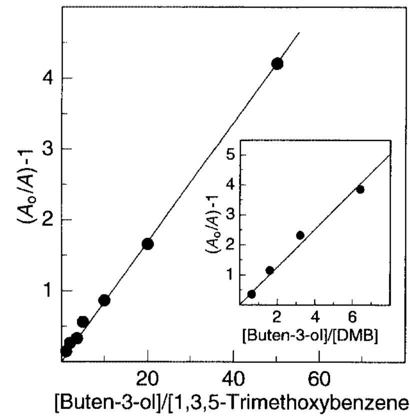

Fig. 2 Competition plot for the reaction of ozone with buten-3-ol and 1,3,5-trimethoxybenzene. The formation of the absorption of 1,3,5-trimethoxybenzene intermediate at 290 nm was the measured entity. Inset: competition plot for the reaction of ozone with buten-3-ol and 1,4-dimethoxybenzene (DMB). The formation of the absorption of 1,4-dimethoxybenzene intermediate at 250 nm was the measured entity.

A competition plot against buten-3-ol, whose rate constant with ozone has been determined[13] at 7.9×10^4 dm^3 mol^{-1} s^{-1}, is shown in Fig. 2 (main graph), and from these data a rate constant of 9.4×10^5 dm^3 mol^{-1} s^{-1} is calculated (for a compilation of rate constants determined in this study see Table 1).

With 1,4-dimethoxybenzene it has been observed that an intermediate is formed which absorbs strongly at 250 nm, where the educt has an absorption minimum ($\varepsilon = 180$ dm^3 mol^{-1} cm^{-1}, data not shown). The kinetics of the formation of this intermediate are again complex (*i.e.* the rate of ozone reaction cannot be derived from these data), and its nature is not yet established. However, its lifetime of >10 s allows us to set up a competition with buten-3-ol (Fig. 2, inset). From these data, one calculates a rate constant of 1.3×10^5 dm^3 mol^{-1} s^{-1} for the reaction of 1,4-dimethoxybenzene with ozone. Thus, the rate constant of ozone with 1,3,5-trimethoxybenzene is more than seven times higher than that of 1,4-dimethoxybenzene. Since ozone is an electrophilic agent,[16] it is expected that the additional methoxy group increases the rate substantially (*cf.* the rate of ozone with anisol is only 2.9×10^2 dm^3 mol^{-1} s^{-1}).[1]

Now, with a competitor at hand which has a rate constant of about 10^6 dm^3 mol^{-1} s^{-1} one can proceed to determine also higher rate constants in competition (propene has a similarly high rate constant,[13] but its use in competition kinetics is very inconvenient). It has been mentioned above that indigotrisulfonate must react faster than 10^7 dm^3 mol^{-1} s^{-1},[7] but the rate constant had not yet been determined. Fig. 3 shows a competition plot with 1,3,5-trimethoxybenzene. The measured

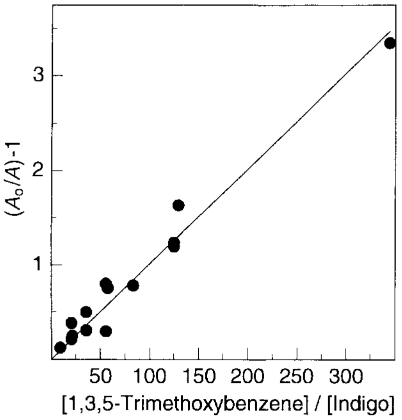

Fig. 3 Competition plot for the reaction of ozone with indigotrisulfonate and 1,3,5-trimethoxybenzene. The bleaching of indigotrisulfonate absorption at 600 nm was the measured entity.

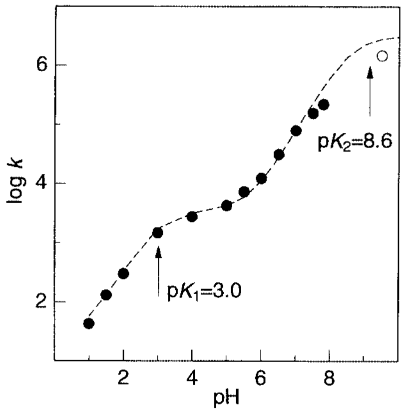

Fig. 4 Plot of the logarithm of the rate constant of the reaction of DABCO with ozone. Data obtained by following the decay of the ozone absorption at 260 nm (●) and by competition (○) using buten-3-ol as competitor.

entity is now the bleaching of indigotrisulfonate. From these data one calculates a rate constant of 9.4×10^7 dm^3 mol^{-1} s^{-1} for its reaction with ozone. This is the highest ozone rate constant ever measured.

It has been mentioned above that amines (and related compounds, *e.g.* amino acids or EDTA[10]) react too fast with ozone to measure the rate of the fully deprotonated compound and that this rate constant has to be derived by extrapolation from measurements at a lower pH.[8,9,17] As an example, the pH dependence of the rate of ozone reaction with DABCO (pK_a values at 3.0 and 8.6) is given in Fig. 4. It can be seen that the fully protonated amine barely reacts with ozone ($k < 30$ dm^3 mol^{-1} s^{-1}), the monoprotonated amine reacts with $k = 3.5 \times 10^3$ dm^3 mol^{-1} s^{-1}, and extrapolation of the data obtained in the basic region yields a rate constant for the fully deprotonated amine of 3.2×10^6 dm^3 mol^{-1} s^{-1}.

The validity of this value can be checked by competition kinetics. In the reaction of ozone with buten-3-ol, formaldehyde is formed according to reactions (5)–(7).[13]

$$\begin{aligned} &HOCH_2\text{–}CH_2\text{–}CH{=}CH_2 + O_3 + H_2O \longrightarrow \\ &\qquad HOCH_2\text{–}CH_2\text{–}CH(OH)OOH + CH_2O + O_2 \quad (5) \end{aligned}$$

$$\begin{aligned} &HOCH_2\text{–}CH_2\text{–}CH{=}CH_2 + O_3 + H_2O \longrightarrow \\ &\qquad HOCH_2\text{–}CH_2\text{–}CHO + HOCH_2OOH + O_2 \quad (6) \end{aligned}$$

$$HOCH_2OOH \longrightarrow CH_2O + H_2O_2 \quad (7)$$

In the reaction of DABCO with ozone, the major product is the *N*-oxide (≈ 90%, singlet oxygen being the other product)[17] and formaldehyde is not formed. Thus, formaldehyde formation can be used to monitor the contribution of the reaction of ozone with buten-3-ol in DABCO–buten-3-ol mixtures. A plot of ($[CH_2O]_0/[CH_2O]$) − 1 *vs.* [DABCO]/[buten-3-ol] yields a straight line (Fig. 5), wherefrom for the reaction of ozone with DABCO at pH 9.5, where these experiments had been carried out, a rate constant of 1.5×10^6 dm^3 mol^{-1} s^{-1} is calculated. At this pH, about 10% of DABCO are still monoprotonated. Extrapolation to fully deprotonated DABCO yields $k = 1.7 \times 10^6$ dm^3 mol^{-1} s^{-1}. This value is also included in Fig. 4.

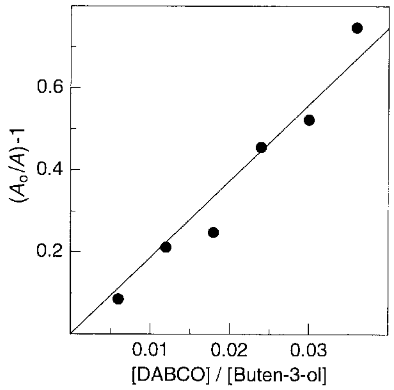

Fig. 5 Competition plot for the reaction of ozone with DABCO and buten-3-ol at pH 9.5. The formation of formaldehyde was the measured entity.

A competition with buten-3-ol (formaldehyde being the measured entity) now also allows us to measure the rate constant of pentachlorophenolate and other halogenated phenolates with ozone.[14] Since these phenols are insoluble, measurements at low pH and extrapolation to high pH is not possible. The value thus obtained for pentachlorophenolate is 1.2×10^6 dm^3 mol^{-1} s^{-1} supporting an earlier statement[8] that this rate constant must be higher than 3×10^5 dm^3 mol^{-1} s^{-1}.

Restrictions in the evaluation of exact ozone rate constants

A considerable problem in determining ozone rate constants is that some product might react orders of magnitude faster with ozone than the substrate. In aqueous solution, this is often the case whenever superoxide radicals are formed (*cf.* refs. 10 and 18). Usually, these do not react with the substrates at any appreciable rate,[19] but react very rapidly with ozone ($k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1})[1] yielding OH radicals *via* the ozonide radical [reactions (8) and (9)].

$$O_2{}^{\bullet -} + O_3 \longrightarrow O_2 + O_3{}^{\bullet -} \quad (8)$$

$$O_3{}^{\bullet -} + H_2O \longrightarrow {}^{\bullet}OH + O_2 + OH^- \quad (9)$$

The OH radicals react very rapidly with the substrates[20] but also with ozone.[20] These and other subsequent free-radical reactions can lead to a noticeable increase in the rate of the ozone decay, and hence an overestimation of rate constants, especially when the observed rate of reaction is low.[10,17] Some improvement may be achieved by scavenging the OH radical by *e.g. tert*-butyl alcohol which does not react with ozone ($k = 0.003$ dm^3 mol^{-1} s^{-1}),[1] but in the subsequent reactions of the ensuing *tert*-butyl alcohol-derived peroxyl radicals further superoxide radicals are released in 25–30% yield.[21] Unfortunately, there are no water-soluble (organic) OH-radical scavengers whose peroxyl radical chemistry does not yield considerable amounts of superoxide either upon their unimolecular or bimolecular decay.[22] The bicarbonate/carbonate system does not have this disadvantage, but in its (rather slow)[20] reaction with the OH radical, the strongly oxidizing $CO_3{}^{\bullet -}$ radical is formed which is capable of reacting with many organic and inorganic compounds.[1]

Another example is the reaction of ozone with secondary amines which produces, among other products, the aminoxyl radical. When this reaction is carried out in water around neutrality, only very little free amine is present in equilibrium, and ozone might react also with the product if its rate constant with ozone is high. A stable, water-soluble aminoxyl radical is TEMPO. Its reaction rate constant with ozone has been determined in competition with indigotrisulfonate (data not shown), and the rate constant thus determined is 1.3×10^7 dm^3 mol^{-1} s^{-1}. As a consequence of this high rate constant, the formation of the stable di-*tert*-butylaminoxyl radical in the reaction of ozone with di-*tert*-butylamine can only be detected in aqueous solution at high pH, where the high reactivity of the unprotonated amine present at higher concentration than in neutral solution (at equal total amine concentration) protects the aminoxyl radical from being rapidly destroyed by ozone.

Acknowledgements

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References

1 P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027.
2 M. L. Kilpatrick and C. D. Herrick, *J. Am. Chem. Soc.*, 1965, **78**, 1784.
3 J. Hoigné, in *The Handbook of Environmental Chemistry*, ed. J. Hrubec, Springer Verlag, Heidelberg, 1998, p. 83.
4 L. Forni, D. Bahnemann and E. J. Hart, *J. Phys. Chem.*, 1982, **86**, 255.
5 H. Bader and J. Hoigné, *Ozone Sci. Eng.*, 1982, **4**, 169.
6 J. Hoigné and H. Bader, *Vom Wasser*, 1980, **55**, 261.
7 H. Bader and J. Hoigné, *Water Res.*, 1981, **15**, 449.
8 J. Hoigné and H. Bader, *Water Res.*, 1983, **17**, 185.
9 W. A. Pryor, D. H. Giamalva and D. F. Church, *J. Am. Chem. Soc.*, 1984, **106**, 7094.
10 F. Muñoz and C. von Sonntag, unpublished results.
11 T. Nash, *Biochem. J.*, 1953, **55**, 416.
12 F. Lipari and S. J. Swarin, *J. Chromatogr.*, 1982, **247**, 297.
13 P. Dowideit and C. von Sonntag, *Environ. Sci. Technol.*, 1998, **32**, 1112.
14 E. Mvula and C. von Sonntag, unpublished results.
15 G. Mark and C. von Sonntag, unpublished results.
16 J. Hoigné and H. Bader, *Water Res.*, 1983, **17**, 173.
17 F. Muñoz, PhD Thesis, Ruhr Universität, Bochum, 1999.
18 F. Muñoz and C. von Sonntag, in preparation.
19 B. H. J. Bielski, D. E. Cabelli, R. L. Arudi and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1041.
20 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
21 M. N. Schuchmann and C. von Sonntag, *J. Phys. Chem.*, 1979, **83**, 780.
22 C. von Sonntag and H.-P. Schuchmann, in *Peroxyl Radicals*, ed. Z. B. Alfassi, Wiley, Chichester, 1997, p. 173.

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