

Singlet dioxygen formation in ozone reactions in aqueous solution

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Florinella Muñoz,[†] Eino Mvula,[‡] Silvia E. Braslavsky and Clemens von Sonntag*

Max-Planck-Institut für Strahlenchemie, Stiftstraße 34–36, PO Box 101365, D-45470, Mülheim an der Ruhr, Germany. E-mail: vonsonntag@mpi-muelheim.mpg.de;
Fax: ++49-(0)208-306-3951; Tel: ++49-(0)208-306-3529

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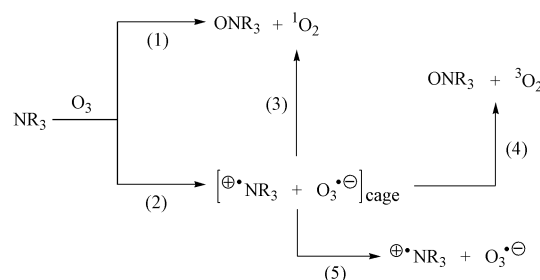
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In ozone reactions, singlet dioxygen [$O_2(^1\Delta_g)$] is formed when ozone reacts by O-atom transfer. $O_2(^1\Delta_g)$ yields were determined for more than 50 compounds using as reference the reaction of hydrogen peroxide with hypochlorite. Close to 100% yields were found in the reaction of O_3 with sulfides, disulfides, methanesulfinic acid, and nitrite. In accordance with this, the only products are: methionine sulfoxide, methanesulfonic acid, and nitrate for the reaction of O_3 with methionine, methanesulfinic acid, and nitrite, respectively. In the case of aliphatic tertiary amines (trimethylamine, triethylamine, and DABCO), the $O_2(^1\Delta_g)$ yields range between 70 and 90%, the aminoxide being the other major product. With EDTA and nitrilotriacetic acid (NTA), the $O_2(^1\Delta_g)$ yield is around 20%. The interpretation of the data with DABCO required the determination of the quenching constant of $O_2(^1\Delta_g)$ by this amine, $k_q = 1.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in H_2O and D_2O , two orders of magnitude lower than previously reported. Aromatic tertiary amines give even lower $O_2(^1\Delta_g)$ yields [*N,N*-dimethylaniline (7%), *N,N,N',N'*-tetramethylphenylenediamine (9%)]. Substantial amounts of $O_2(^1\Delta_g)$ are also formed with the DNA model compounds, 2'-deoxyguanosine (40%) and 2'-deoxyadenosine (15%, in the presence of *tert*-butyl alcohol as $\cdot OH$ scavenger). The pyrimidine nucleobases only yield $O_2(^1\Delta_g)$ when deprotonated at N(1). $O_2(^1\Delta_g)$ formation is also observed with hydrogen sulfide (15%), azide (17%), bromide (56%), iodide (12%), and cyanide ions (20%). The $O_2(^1\Delta_g)$ yield from the reaction of O_3 with phenols and phenolates is typically around 20%, but may rise closer to 50% in the case of pentachloro- and pentabromophenolate. Low $O_2(^1\Delta_g)$ yields are found with unsaturated acids such as dihydroxyfumarate (6%), muconate (2%), and acetylenedicarboxylate (15%). With saturated compounds, also, no $O_2(^1\Delta_g)$ (e.g. with propan-2-ol, acetaldehyde, acetaldehyde dimethylacetal and glyoxal) or very little $O_2(^1\Delta_g)$ (formic acid; 6%, at high formate concentrations) was detected. As shown with some examples, knowledge of the $O_2(^1\Delta_g)$ yield (in combination with that of other products) is a prerequisite for the elucidation of the mechanisms of O_3 reactions in aqueous solutions.

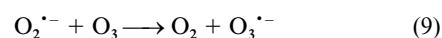
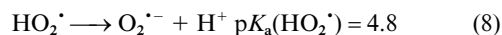
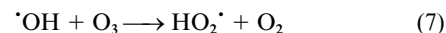
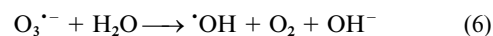
It is well-known that in O_3 reactions singlet dioxygen [$O_2(^1\Delta_g)$] may be formed in high yields.^{1,2} This is always the case when O-transfer reactions dominate. Spin conservation rules then demand that the resulting dioxygen molecule must be in its (excited) singlet state, because educt and O_3 as well as the product are in their singlet (ground) states. A case in point is the reaction of O_3 with tertiary amines, whereby aminoxides are generated [reaction (1)].^{3–6}

In water, the reactions of O_3 may differ considerably from those encountered in the gas phase and in organic solvents (*cf.* ref.7 and 8). Moreover, the high permittivity of water may allow electron-transfer reactions to occur [*e.g.* reaction (2)] which are not possible in an organic solvent due to the lower solvation energies of the resulting radical ions.

In water, the energy gained upon solvation of the resulting ions reduces the ionization potential by about 3 eV as compared to the gas phase ionization potential, while in an organic solvent only 1 to 2 eV are gained.^{9,10} Since the electron affinity of O_3 is only 2.1 eV,¹¹ such an electron-transfer reaction will, even in water, only be possible with molecules that have a low ionization potential (a recent suggestion¹² to revise the currently accepted mechanism of O_3 reactions has therefore to be rejected). However, should electron transfer occur [*cf.* reaction (2)], ensuing free-radical reactions would lead also to the O-transfer product [*e.g.*, reactions (3) and (4)], but the



ratio of the $O_2(^1\Delta_g)$ yield and the O-transfer-product yield may fall below unity [*cf.* reaction (4)]. Upon diffusing out of the cage [reaction (5)], the ozonide radical can induce a decomposition of the O_3 via a chain reaction [reactions (6)–(9)].



In competition, the ensuing OH radicals formed in reaction (6) also attack the substrate.

Ozone is widely used in drinking-water processing, but the O_3 reactions in water are as yet not adequately understood. In most studies, material balances are missing, and the formation

[†] Present address: Escuela Politécnica Nacional, Instituto de Ciencias Nucleares, Quito, Ecuador.

[‡] On leave from Department of Chemistry, University of Namibia, Windhoek, Namibia.

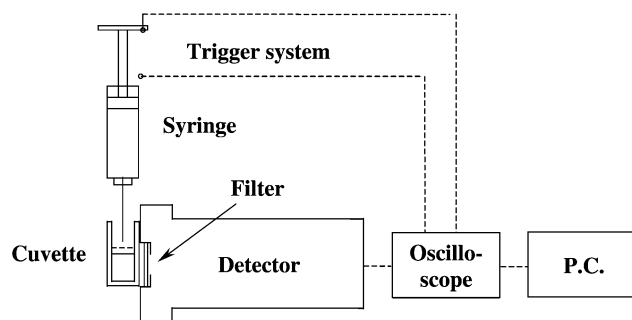


Fig. 1 Schematic representation of the $\text{O}_2(^1\Delta_g)$ detection system

of $\text{O}_2(^1\Delta_g)$ may give important information, besides mechanistic aspects, on the formation of potential products that have escaped attention. For this reason, we attempted to quantify the $\text{O}_2(^1\Delta_g)$ yields in a number of systems relevant to drinking-water processes, notably EDTA and related complexing agents.^{6,13} This study was then put on a wider footing, *e.g.* with sulfur-containing compounds, phenols, inorganic ions, and DNA constituents.

In the determination of the $\text{O}_2(^1\Delta_g)$ yield in aqueous solutions, a number of problems may arise as has been pointed out by Kanofsky and his group in their pioneering work.¹ Here, we will report on some additional complications, but will show that, despite the difficulties, useful data may be obtained.

Experimental

All chemicals were of the highest purity commercially available. Ozone solutions were made-up in Milli-Q-purified (Millipore) water using an O_2 -fed ozonator (SWO-70, WEDECO). Ozone concentrations were determined spectrophotometrically taking $\epsilon(260 \text{ nm}) = 3314 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.¹⁴

The set-up used in the present study consists of a liquid N_2 -cooled germanium photodiode (EO-817L, North Coast Scientific Corporation, rise time 5–10 ms) sensitive to the 1270 nm phosphorescence emitted by $\text{O}_2(^1\Delta_g)$. In front of the detector, a Suprasil quartz cell ($1 \times 1 \text{ cm}$), a bandpass filter ($1270 \pm 70 \text{ nm}$, Laser Components) and a silicon cut-off filter ($< 1050 \text{ nm}$, Laser Components) were placed at a distance of one cm (see Fig. 1). The signal was electrically triggered simultaneously with the injection of the substrate solution, recorded by a storage oscilloscope (Tektronix 2221A), and the data were evaluated with the help of laboratory-produced software.

Ozone rate constants were determined by competition (*cf.* ref. 15) using buten-3-ol ($k = 7.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)⁷ as competitor. The measured entity is formaldehyde which was determined by the Hantzsch reaction.¹⁶

Methionine and its sulfoxide were separated by HPLC on a 15 cm C-18 reversed phase column using water as eluent (retention times 5 and 3.6 min, respectively).

The product of the ozonation of *trans*-1,2-dithiane-4,5-diol were identified by GC/MS after trimethylsilylation. There is only one product, and its mass spectrum is compatible with that of bis-TMS ether of 1-oxo-1 λ^4 -1,2-dithiane-4,5-diol (MW 312); m/z (%): 312 (1), 297 (3), 217 (17), 204 (3), 196 (19), 180 (4), 147 (72), 133 (22), 116 (90), 101 (34), 73 (100). ^1H NMR (D_2O): $\delta = 4.17$ (ddd; $J = 11.5, 9.4, 3.6 \text{ Hz}$; $5\alpha\text{-H}$), 3.89 (ddd; $J = 10.9, 9.4, 3.7 \text{ Hz}$; $4\beta\text{-H}$), 3.73 (dd; $J = 13.5, 3.6 \text{ Hz}$; $6\alpha\text{-H}$), 3.44 (dd; $J = 14, 10.9 \text{ Hz}$; $3\alpha\text{-H}$), 3.17 (dd; $J = 13.5, 11.5 \text{ Hz}$; $6\beta\text{-H}$), 3.14 (dd; $J = 14, 3.7 \text{ Hz}$; $3\beta\text{-H}$). For comparison, the mass spectrum of the bis-TMS ether of *trans*-1,2-dithiane-4,5-diol (MW 296) shows a similar pattern as concerns the major fragmentation pathway; m/z (%): 296 (26), 281 (1), 203 (13), 180 (82), 147 (58), 133 (11), 116 (100), 101 (25), 73 (86). ^1H NMR (D_2O): $\delta = 3.59$ (m; 4-H, 5-H), 3.09 (br d; $J = 13.3 \text{ Hz}$; one 3-H, one 6-H), 2.88

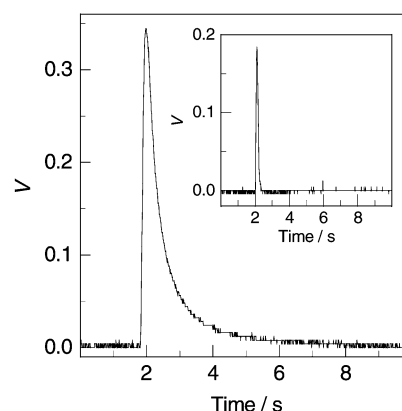


Fig. 2 Signals of $\text{O}_2(^1\Delta_g)$ emission during the reaction of H_2O_2 with HOCl ($7.5 \times 10^{-4} \text{ mol dm}^{-3}$ each). Inset: signals of $\text{O}_2(^1\Delta_g)$ emission in the reaction of O_3 ($1 \times 10^{-4} \text{ mol dm}^{-3}$) with EDTA ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$). Measurements in H_2O .

Table 1 Integrated emission of $\text{O}_2(^1\Delta_g)$ in the reference system ($\text{H}_2\text{O}_2 + \text{NaOCl}$)

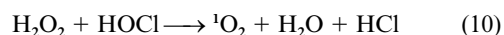
Run	Area
1	0.3386
2	0.3420
3	0.3101
4	0.3352
5	0.3242
6	0.2875
7	0.2737
8	0.2965
9	0.2898
10	0.3200
X	0.3118 ± 0.024

(dd; $J = 13.3, 9.2 \text{ Hz}$; one 3-H, one 6-H), in agreement with reported¹⁷ data.

Results and discussion

Determination of $\text{O}_2(^1\Delta_g)$ yields

The arrangement shown in Fig. 1 allowed us to carry out the experiments in H_2O despite the fact that the photon yield is low due to the intrinsic $\text{O}_2(^1\Delta_g)$ lifetime of only 3–4 μs in this solvent.¹⁸ A volume of 1.2 ml of an O_3 solution of known concentration (determined spectrophotometrically, see Experimental section) was placed in the cuvette and 0.4 ml of the substrate solution (containing buffer if required) injected at the bottom of the cuvette. As a reference, the formation of $\text{O}_2(^1\Delta_g)$ from the reaction of hydrogen peroxide with hypochlorite [reaction (10)] was used, and its quantum yield was taken as unity (*cf.* also ref. 1 and 2).



It is unavoidable that there are volumes within the cuvette, from where the emissions do not reach the photodiode. Should complete mixing be achieved before a major advance of the reaction, this does not matter because only a fraction of the emitted light is recorded anyway. However, when the mixing is incomplete the reaction can, to a certain extent, preferentially take place in volumes seen (or not seen) by the detector. The recorded emission will thus be higher (or lower) than it would be for homogeneous mixing. This situation leads to considerable scatter of the data even in the case of the slow¹⁹ H_2O_2 – HOCl reaction (*cf.* Fig. 2, main graph), but signal-averaging over a reasonable number of runs improves the quality of the data (*cf.* Tables 1 and 2). However, when the rate

Table 2 Integrated emission of $O_2(^1\Delta_g)$ in the reaction of O_3 with EDTA ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$, pH 4.5)

Run	$[O_3]/10^{-4} \text{ mol dm}^{-3}$	Area	$[O_2(^1\Delta_g)]/10^{-5} \text{ mol dm}^{-3}$	% $O_2(^1\Delta_g)$
1	2.26	0.0208	5.00	22.1
2	2.20	0.0227	5.45	24.8
3	2.13	0.0230	5.52	26.0
4	2.04	0.0253	6.09	29.9
5	1.99	0.0227	5.45	27.4
6	1.92	0.0292	7.03	36.5
7	1.72	0.0254	6.10	35.5
X				28.9 ± 5.4

of reaction becomes very fast as in the O_3 -EDTA reaction (cf. inset in Fig. 2), complete mixing is not achieved within the short reaction time, and hence the error becomes noticeably larger.

On the other hand, when the reaction becomes very slow, the signal may disappear in the noise. A case in point is amines where only the free base is reactive toward O_3 , and thus the rate of reaction strongly depends on the pH (cf. ref. 15). Thus, at low amine concentrations and/or a pH quite distant from the pK_a , the $O_2(^1\Delta_g)$ signal may become small or disappear altogether. Further errors result from the instability of the aqueous O_3 stock solution. Therefore, repeated measurements of its O_3 content were required. The $O_2(^1\Delta_g)$ yields were determined by integrating the areas under the signal (in volts) vs. time curves (cf. Fig. 2) and are given in Table 3. They are based on the average H_2O_2 -HOCl- reference value (cf. Table 1), and the error given is only the statistical error of the measurements for the individual compounds (cf. Table 2).

The $O_2(^1\Delta_g)$ yields from the O_3 reactions with a large number of compounds are compiled in Table 3. At an O_3 : substrate ratio = 1, the measured $O_2(^1\Delta_g)$ yield is often very low. This can be rationalized if there are fast free-radical processes causing chain reactions which consume both O_3 and the substrate. In addition, the reaction may become so slow that the signal disappears within the noise. Thus, only values for a ten-fold substrate concentration may be used with some confidence. However, often the low solubility of the substrate did not allow the use of high concentrations.

Quenching of $O_2(^1\Delta_g)$ by the substrate

Amines are known to be good $O_2(^1\Delta_g)$ quenchers. A large number of rate constants for $O_2(^1\Delta_g)$ reactions have been compiled,¹⁸ but relatively few rate constants have been measured in aqueous solutions. The value reported for $O_2(^1\Delta_g)$ quenching by DABCO in aqueous solution is $2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,²⁰ as derived from the analysis of a rather complex sequence of reactions. Should this value be indeed that high, we would have observed a substantial drop in the $O_2(^1\Delta_g)$ yields at high DABCO concentrations. This not being the case, a redetermination of the $O_2(^1\Delta_g)$ quenching rate constant by a more direct method was required. We produced $O_2(^1\Delta_g)$ by the H_2O_2 -HOCl reaction (see above) and measured the $O_2(^1\Delta_g)$ yields as a function of the DABCO concentration, both in H_2O and in D_2O . Since the lifetime of $O_2(^1\Delta_g)$ is much longer in D_2O than in H_2O [$k(\text{in } H_2O) \approx 3 \times 10^5 \text{ s}^{-1}$, $k(\text{in } D_2O) \approx 1.8 \times 10^4 \text{ s}^{-1}$],¹⁸ quenching of $O_2(^1\Delta_g)$ in D_2O must occur at much lower DABCO concentrations than in H_2O . This is indeed observed (Fig. 3). The $O_2(^1\Delta_g)$ quenching rate constant in H_2O and in D_2O is calculated as $k_q = 1.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

This value is two orders of magnitude lower than the previously reported one. Our low value of $O_2(^1\Delta_g)$ quenching by DABCO now explains why no significant reduction of $O_2(^1\Delta_g)$ yields was found in the O_3 reactions at high DABCO concentrations (see Table 3).

Similar experiments were carried out with azide (data not shown), and its $O_2(^1\Delta_g)$ quenching rate constant was found to be $9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which compares well with the data

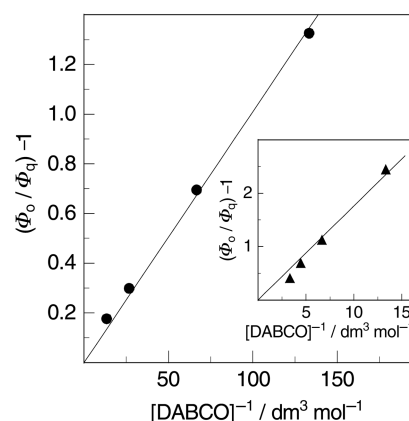


Fig. 3 Stern-Volmer plots for the quenching of $O_2(^1\Delta_g)$ by DABCO in H_2O (main graph) and D_2O (inset). $O_2(^1\Delta_g)$ was generated by the reaction of H_2O_2 with HOCl (each $7.5 \times 10^{-4} \text{ mol dm}^{-3}$ in H_2O and $7.5 \times 10^{-5} \text{ mol dm}^{-3}$ in D_2O). Solutions were basic due to the high concentration of DABCO.

from the literature which range from $5.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (for a compilation see ref. 18).

Although this approach worked fine in the case of DABCO and azide, a cautionary remark needs to be made. The H_2O_2 -HOCl reaction may not always be a good $O_2(^1\Delta_g)$ source for quenching experiments whenever either HOCl or H_2O_2 (or both) reacts rather fast with the quencher under study. In our hands, this seemed to be the case with several amines (but not with DABCO).

Some mechanistic aspects

Amines. In the case of tertiary amines the formation of $O_2(^1\Delta_g)$ is connected with the formation of the aminoxide, mainly reaction (1), although contributions of reaction (3) may also play a small role (for studies in organic solvents see refs. 3,4,21–23; in the gas phase the postulated aminoxide intermediate further decomposes²⁴). Due to a potential contribution of reaction (4), the yield of $O_2(^1\Delta_g)$ may be slightly lower than that of the aminoxide.⁶ In the case of trimethylamine and triethylamine, the products resulting from the reactions following reaction (5), i.e. the corresponding dialkylamines and aldehydes, complete the material balance.^{6,13} Only the free amine reacts with O_3 , and the protonated amine does not show any reactivity.^{6,13,15,25,26} Thus, when most of the amine is protonated (e.g. at pH 7) the rate of reaction slows down (at equal total amine concentration). As a consequence, the chain reactions induced by the free-radical pathway consume both O_3 and amine and hence reduce the yield of $O_2(^1\Delta_g)$. Here, it is of interest that not only the ozonide radical may start the chain but also the amine radical cation (cf. studies on trimethylamine²⁷ and EDTA²⁸).

In the case of the aromatic tertiary amines, *N,N*-diethyl-aniline and *N,N,N',N'*-tetramethylphenylenediamine, the yield of $O_2(^1\Delta_g)$ is comparatively low (<10%, cf. Table 3). These aromatic tertiary amines have lower reduction potentials than

Table 3 $\text{O}_2(^1\Delta_g)$ yields in O_3 reactions in % of O_3 consumed at different pH and at various substrate : O_3 ratios (in parentheses). The data are average values of at least five individual determinations (scatter less than $\pm 15\%$). The O_3 concentrations in these experiments were typically $(1-2) \times 10^{-4} \text{ mol dm}^{-3}$

Substrate	pH	Yield (%) (substrate : ozone)
Trimethylamine	7	63 (10 : 1)
	9.5	60 (10 : 1), 69 (100 : 1)
Triethylamine	7	No signal (1 : 1), 42 (10 : 1), 72 (10 : 1)
	8	No signal (1 : 1), 63 (10 : 1), 80 (100 : 1)
	9.5	52 (1 : 1), 73 (10 : 1), 85 (100 : 1)
	10.5	59 (1 : 1)
	11.5	78 (100 : 1)
DABCO	7	70 (1 : 1), 80 (10 : 1)
	9	90 (10 : 1)
EDTA	4.5	No signal (1 : 1), 19 (10 : 1)
	5.5	No signal (1 : 1), 40 (10 : 1), 39 (100 : 1)
	7	39 (1 : 1), 59 (10 : 1), 43 (100 : 1)
	9.5	31 (1 : 1), 33 (10 : 1), 37 (100 : 1)
EDTA- Ca^{2+}	~3	15 (10 : 1)
EDTA- Fe^{3+}	~3	No signal (1 : 1), no signal (10 : 1)
Nitrilotriacetic acid (NTA)	7	No signal (1 : 1), 18 (10 : 1)
	9.5	22 (1 : 1), 21 (10 : 1)
Diethylamine	9	20 (1 : 1)
	10.5	24 (1 : 1), 20 (10 : 1)
Iminodiacetic acid (IDA)	9	17 (1 : 1)
	10.5	20 (1 : 1), 18 (10 : 1)
Ethylamine	9	No signal (1 : 1)
	10.5	11 (1 : 1), 17 (10 : 1)
Glycine	7	No signal (1 : 1), (10 : 1)
	10.5	4 (10 : 1)
<i>N,N</i> -Diethylaniline	8.5	7 (17 : 1)
<i>N,N,N',N'</i> -Tetramethylphenylenediamine	3.5	9 (3 : 1)
	6	4 (3 : 1)
Uracil	3.5	No signal (9 : 1)
	7	6 (9 : 1)
	11	7 (9 : 1)
1,3-Dimethyluracil	3.5	No signal (4 : 1)
	11	No signal (4 : 1)
6-Methyluracil	3.5	No signal (10 : 1)
	7	12 (10 : 1)
	10	15 (10 : 1)
5-Chlorouracil	3.5	No signal (4 : 1)
	7	45 (4 : 1)
	11	43 (4 : 1)
Thymine	3.5	No signal (4 : 1)
	7	4 (4 : 1)
	10	8 (4 : 1)
Thymidine	7	No signal (10 : 1)
	10	No signal (4 : 1)
Cytosine	7	No signal (16 : 1)
	11	10 (16 : 1)
2'-Deoxycytidine	7	No signal (10 : 1)
Cytidine	7	No signal (10 : 1)
2'-Deoxyguanosine	7	40 (10 : 1)
Guanosine	7	37 (1 : 1)
2'-Deoxyadenosine ^b	7	16 (10 : 1)
Adenosine ^b	7	10 (1 : 1), 21 (10 : 1)
Phenol	1.8	No signal (10 : 1)
	7	6 (10 : 1)
	9	9 (10 : 1)
	10	8 (10 : 1)
Tyrosine	7	9 (1 : 1), 12 (1 : 1) ¹
2,4,6-Trimethylphenol	7	10 (1 : 1)
	9	17 (10 : 1)
Pentachlorophenol	8	58 (1 : 1), 68 (10 : 1)
Pentabromophenol	8	48 (1 : 1), 59 (10 : 1)
2,4,6-Triiodophenol	9	19 (10 : 1)
1,4-Dimethoxybenzene	7	6 (1 : 1)
1,3,5-Trimethoxybenzene	7	30 (1 : 1)
Nitrite	7	96 (100 : 1)
Azide	7	11 ^a (1 : 1)
Cyanide	> 11	21 (10 : 1)
Bromide	7	Weak broad signal (40 : 1), 56 (400 : 1)
Iodide	7	12 (3 : 1)
Hydrogen sulfide	7	16 (100 : 1)
	11	15 (100 : 1)
Methanesulfinate	10	96 (1.4 : 1)
Formate	7	Weak signal (23 : 1), 6 (230 : 1)
Glyoxylate	7, 11	No signal (25 : 1)
Dihydroxyfumarate	7	6 (23 : 1)

Table 3 (Contd.)

Substrate	pH	Yield (%) (substrate : ozone)
Muconate	10	2 (100 : 1)
Acetylenedicarboxylate	10	Weak signal (100 : 1), 15 (1000 : 1)
1,4-Dithiothreitol	4.8	46 (38 : 1)
	7	22 (38 : 1)
	9	17 (38 : 1)
<i>trans</i> -1,2-Dithiane-4,5-diol	7	105 (31 : 1)
Methionine	7	104 (42 : 1)
Glyoxal	7, 11	No signal (25 : 1)
Acetaldehyde	7	No signal (1000 : 1)
Acetaldehyde dimethylacetal	7	No signal (1000 : 1)
Propan-2-ol	7	No signal (500 : 1)

^a Not corrected for quenching by substrate; upon correction the value is 17%. ^b In the presence of *tert*-butyl alcohol.

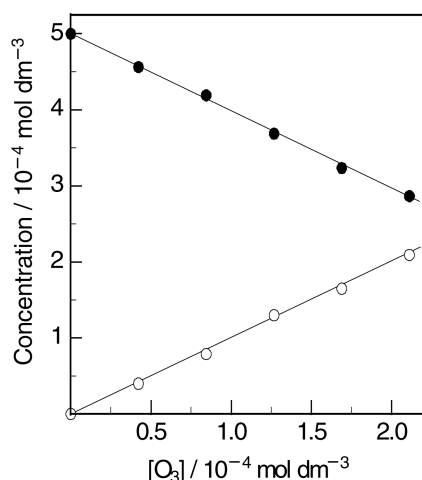
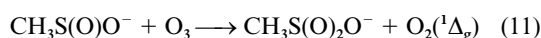


Fig. 4 Reaction of ozone with methionine at pH 3. Consumption of methionine and formation of its sulfoxide as a function of the ozone concentration.

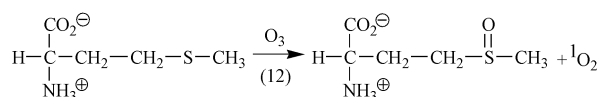
the aliphatic ones [e.g., *E*(*N,N*-dimethylaniline) ≈ 0.770 V, *E*(*N,N,N',N'*-tetramethylphenylenediamine) = 0.265 V],²⁹ and most probably the electron-transfer process becomes the major process [*E*($O_3/O_3^{\cdot-}$) = 1.01 V].²⁹

Sulfur-containing compounds. The methanesulfinate ion reacts rapidly with O_3 by O-transfer to give methanesulfonate and $O_2(^1\Delta_g)$ [reaction (11); $k = 2 \times 10^6$ dm³ mol⁻¹ s⁻¹].³⁰ An



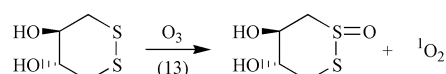
electron-transfer reaction that would give rise to a very efficient chain reaction is not observed.³⁰

The sulfide methionine reacts very fast with O_3 ($k = 1.8 \times 10^6$ dm³ mol⁻¹ s⁻¹),²⁶ the $O_2(^1\Delta_g)$ yield being practically 100% (cf. Table 3 and ref. 2) [reaction (12)]. Its sulfoxide has been



reported as the only detected product,³¹ and we find that the methionine sulfoxide yield is indeed 100% (Fig. 4).

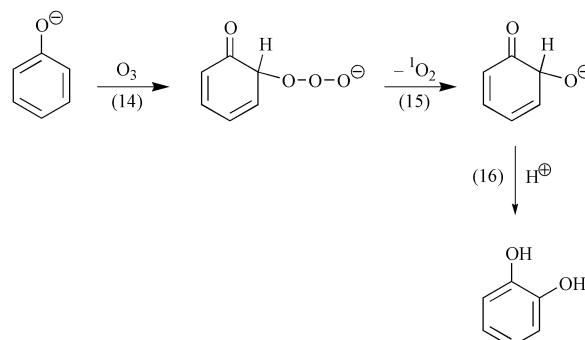
The disulfide *trans*-1,2-dithiane-4,5-diol in its reaction with O_3 also gives rise to 100% $O_2(^1\Delta_g)$ [cf. reaction (13); $k = 2.1 \times 10^5$ dm³ mol⁻¹ s⁻¹].



This reaction is notably faster than the rate constant of O_3 with cystine for which a value of 550 dm³ mol⁻¹ s⁻¹ has been reported.²⁵ In order to see whether the reaction of *trans*-1,2-dithiane-4,5-diol is unusually high, we also determined the rate constant for bis(2-hydroxyethyl) disulfide and find a value of 1.7×10^5 dm³ mol⁻¹ s⁻¹ for this disulfide, *i.e.* we have no explanation for the low rate of reaction observed with cystine. In both cases, the final products are the corresponding *S*-alkyl sulfonates, corroborating that the O_3 reaction proceeds by O-transfer.

Compared with sulfides and disulfides, thiols show relatively low $O_2(^1\Delta_g)$ yields (< 50%), especially when deprotonated [$pK_a(H_2S) = 7.0$; $pK_a(1,4$ -dithiothreitol) = 9.1, 10.5]. Thiols react much more readily with ozone than thiols,²⁵ and changes in $O_2(^1\Delta_g)$ yields are already observed in a pH range where the thiol still predominates. A case in point is 1,4-dithiothreitol which already shows a strong drop in the $O_2(^1\Delta_g)$ yield on going from pH 4.8 to 7. This low $O_2(^1\Delta_g)$ yield has, of course, a bearing on the reactions of O_3 with *e.g.* H_2S , where it has been noted that sulfate is formed as the only detectable product. Interestingly, this reaction requires only ~ 2.3 mol O_3 per mol H_2S .^{32,33} This stoichiometry requires that an efficient chain reaction must occur (for an EPR study on the reactions of dioxygen with $HS^{\cdot-}$ and $S^{\cdot-}$ with O_2 see ref. 34).

Phenols. Phenolate reacts as much as six orders of magnitude faster with O_3 than phenol.²⁵ Thus, even at pH ~ 7 (especially in the presence of a buffer that re-establishes the equilibrium upon phenolate depletion) the phenolate [$pK_a(\text{phenol}) = 10$] is the dominating reactant. No $O_2(^1\Delta_g)$ has been observed in the reaction of phenol at pH 1.8, *i.e.* the formation of $O_2(^1\Delta_g)$ at pH 7 is likely due to a reaction with the phenolate present in the equilibrium. Much higher $O_2(^1\Delta_g)$ yields are observed with the halogenated phenolates. In view of its importance in water purification, the ozone chemistry of phenol has been widely studied,³⁵⁻⁴⁸ but it is not yet fully understood. At present, one can only speculate on the nature of the products that may be formed in the course of $O_2(^1\Delta_g)$ release, although catechol and hydroquinone are the most likely ones [cf. reactions (14)–(16)]. These products are indeed formed, but

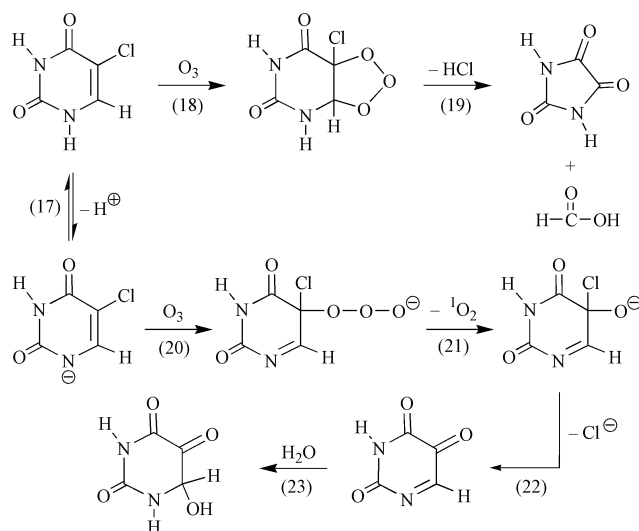


largely originate from a chain reaction involving $\cdot\text{OH}$ as intermediates.⁴⁹

The ozone⁵⁰ and $\cdot\text{OH}$ -induced⁵¹ chemistry of halogenated phenols has also been studied, but the analysis of the products is even more difficult in these systems. A material balance has not been achieved.

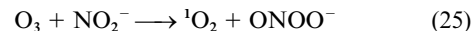
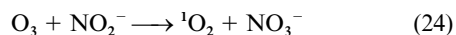
Phenols quench $\text{O}_2(^1\Delta_g)$ with rate constants of $\sim 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁵² This low quenching rate will not influence our $\text{O}_2(^1\Delta_g)$ yield at pH 7. Upon deprotonation, the quenching rate constant is raised to $1.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, *i.e.* quenching still has no effect at pH 9, but may have lowered our pH 10 value slightly.

DNA constituents and related compounds. A considerable effect of pH on the rate of the reaction of O_3 with the nucleobases and related compounds has recently been reported.⁵³ Here, we show that this may be connected with a change in mechanism, *i.e.* the $\text{O}_2(^1\Delta_g)$ yield may become quite pronounced at high pH where the nucleobase is deprotonated. The most striking example is 5-chlorouracil (*cf.* Table 1). We suggest that when the neutral molecule predominates, the ozone reaction follows the Criegee mechanism [overall reactions (18) and (19)], but upon deprotonation [reaction (17)] an isopyrimidine^{54,55} is formed [reaction (20)]. Preliminary experiments indicate that 5-chlorouracil indeed yields HCl, parabanic acid (imidazolidine-trione), and formic acid [reaction (19)], whereas in the reaction of the 5-chlorouracilate ion with ozone the yields of parabanic acid and formic acid are reduced and isodialuric acid (dihydro-6-hydroxypyrimidine-2,4,5(3*H*)-trione) is formed instead [reactions (20)–(23)].⁵⁶



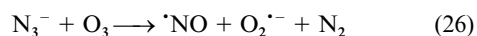
Compared to the other nucleobases, the rate of the reaction of adenine and its derivatives with O_3 is slow, and OH radicals are formed (possibly *via* superoxide radicals as intermediates). To suppress subsequent reactions, *tert*-butyl alcohol was added as $\cdot\text{OH}$ -scavenger in order to measure the intrinsic $\text{O}_2(^1\Delta_g)$ as accurately as possible. The formation of $\text{O}_2(^1\Delta_g)$ is an indication that an O-transfer reaction must occur, but in the reaction of 2'-deoxyadenosine the *N*¹-oxide is not formed to a noticeable extent,⁵⁷ indicating that an O-transfer to N(1) does not occur (this is the position of *N*-oxide formation by hydrogen peroxide, *cf.* ref. 58). The reaction leading to $\text{O}_2(^1\Delta_g)$ is thus not yet known. This also holds for guanosine.

Nitrite and azide ions. In its reaction with O_3 , the nitrite ion gives rise to $\text{O}_2(^1\Delta_g)$ in $\sim 100\%$ yield. In principle, one may envisage two pathways of O-transfer, one leading to nitrate [reaction (24)], the other to peroxynitrite [reaction (25)]. The

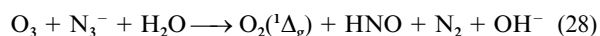


observation that peroxynitrite is not formed ($< 2\%$)⁵⁹ is in good agreement with the thermochemistry of these two reactions [reaction (25) is endothermic].

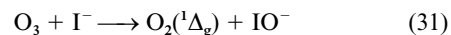
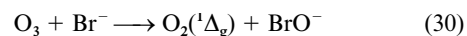
The reaction of O_3 with azide has attracted some attention^{60–62} because of the formation of peroxynitrite in this system.^{61,62} No N_2 has been found among the reaction products.⁶¹ For the formation of peroxynitrite, this has led to the suggestion of a two-step process. In the first step, N_2O and an NOO^- species are thought to be formed. The reaction of the latter with a second molecule of O_3 would then give peroxynitrite [and $\text{O}_2(^1\Delta_g)$; the postulated NOO^- species cannot be identical with nitrite which gives rise to nitrate and not peroxynitrite, see above]. This mechanism has to be disregarded because the reaction of O_3 with azide is fast ($k = 4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)⁶³ and peroxynitrite builds up without an induction period even at an azide concentration of 0.1 mol dm^{-3} .⁶¹ Considering that no material balance has as yet been obtained,⁶¹ the N_3^- – O_3 system has to be re-investigated, and the question of N_2 formation has to be re-addressed. Were it a major product, peroxynitrite should be formed according to reactions (26) and (27), compatible with what we know now about the formation



and decay of this species (*cf.*, *e.g.*, ref. 64). The formation of $\text{O}_2(^1\Delta_g)$ and N_2O , for which there is no adequate explanation as yet, could also be reconciled by the sequence (28) and (29). O-transfer to azide may lead to HNO [reaction (28)] which is a well-known precursor of N_2O [reaction (29)].



Bromide and iodide ions. In its reaction with Br^- , $\text{O}_2(^1\Delta_g)$ is produced in a $\sim 50\%$ yield [reaction (30)], and in the case of I^- the $\text{O}_2(^1\Delta_g)$ yield is only $\sim 12\%$ [reaction (31)].



Reaction (30) is currently considered to be the only primary process occurring in the Br^- system.^{65–69} Since Br^- and I^- are poor $\text{O}_2(^1\Delta_g)$ quenchers [$k(\text{Br}^-) = 1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $k(\text{I}^-) = 7.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$],¹⁸ it is difficult to see why the $\text{O}_2(^1\Delta_g)$ yields should not reach 100%. Despite this, one may consider that an O_3 – Br^- -adduct, the *bona-fide* intermediate in reaction (30), is sufficiently long-lived to reduce the $\text{O}_2(^1\Delta_g)$ yield by spin conversion due to the heavy atom effect caused by the bromine atom. In the corresponding reaction with I^- , such a heavy atom effect should be even more pronounced. Indeed, the $\text{O}_2(^1\Delta_g)$ yield is even lower in this system. However, these low $\text{O}_2(^1\Delta_g)$ yields also raise the question of whether there are additional free-radical pathways in these systems. This question is currently under investigation in our laboratory. The reaction of O_3 with I^- is one of the standard methods for measuring O_3 concentrations. In this assay, I_2 is determined.^{70–72} Its yield has been in dispute, *cf.* ref. 73, although there now seems to be general agreement that the stoichiometry is 1:1. The low $\text{O}_2(^1\Delta_g)$ yield found in this study may be the basis for studying again the mechanistic details of this interesting and certainly complex reaction.

Cyanide ion. In the cyanide– O_3 system cyanate is practically the only product, but besides the O-transfer which leads to

$O_2(^1\Delta_g)$ there are two chain reactions (one can be interrupted by *tert*-butyl alcohol, the other one cannot).⁷⁴ Thus, the $O_2(^1\Delta_g)$ yields given in Table 3 only reflect its yields under very specific experimental conditions.

Saturated compounds. The reactions of ozone with saturated compounds are still poorly understood. In the case of propan-2-ol (neat or in an organic solvent) O_3 evolves when ozone reacts at low temperatures⁷⁵ and some 3% of $O_2(^1\Delta_g)$ is detected in the presence of an $O_2(^1\Delta_g)$ probe.⁷⁶ Due to incomplete scavenging of $O_2(^1\Delta_g)$ under these conditions, this must be a lower value. In aqueous solution, the O_3 reaction may proceed with free radicals as intermediates,⁷⁷ but this has not been reported for propan-2-ol.⁷⁸ Hydrotrioxides are expected intermediates.^{79,80} Such intermediates may also account for the pronounced selectivity of the ozone reaction with D-glucose in the presence of an 1OH scavenger.⁸¹ In a recent study on the reaction of propan-2-ol with ozone in organic solvents and at low temperatures, the formation of the hydrotrioxides $(CH_3)_2C(OH)OOH$ and $HOOOH$ has now been established by ^{17}O NMR.⁸² Furthermore, it has been shown that the decay of these species is catalysed by water. These experiments were carried out at 0 °C in deuterated acetone up to a water content of 4 mol dm⁻³. It is very daring to extrapolate these data to neat water (55 mol dm⁻³) and to room temperature, yet the low rate of the decay of the hydroperoxides under their conditions does not exclude the possibility that the lifetimes of these hydroperoxides may be longer than the few seconds required for an adequate determination of the $O_2(^1\Delta_g)$ signal (cf. Fig. 2). However, the information available from radiation-chemical studies on the properties of $HOOOH$ suggests a sufficiently short lifetime.^{83,84} The (water-catalysed) decay of $(CH_3)_2C(OH)OOH$ and $HOOOH$ is expected to give rise to $O_2(^1\Delta_g)$. Thus, the fact that we were unable to detect any $O_2(^1\Delta_g)$ is very intriguing.

Conclusions

Through product analysis, we have shown that upon reaction of O_3 with methionine, methanesulfinic acid and nitrite O-transfer is the only reaction. In these cases, the $O_2(^1\Delta_g)$ yield is also 100%, *i.e.* material balance is obtained. This not only indicates that our $O_2(^1\Delta_g)$ yield measurements can be used with some confidence within the limitations discussed above, but that $O_2(^1\Delta_g)$ yields provide most valuable information as to mechanistic details of ozone reactions in aqueous solution and certainly also in non-aqueous solvents. Thus, the determination of $O_2(^1\Delta_g)$ yields is an indispensable tool in mechanistic studies of ozone reactions in general. The ease of such experiments and the relatively low equipment cost may stimulate a more abundant use of this technique.

Acknowledgements

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