J. Chem. Research (S), 1997, 172–173†

Kinetics of the Reactions of $O^{\bullet -}$ and $HO^{\bullet}$ with α,α,α-Trifluorotoluene and 4-Fluorotoluene†

Laura S. Villata, Janina A. Rosso, Mónica C. Gonzalez* and Daniel O. Mártire*‡

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Casilla de Correo 16, sucursal 4, (1900) La Plata, Argentina

The absolute rate constants for the reactions of $O^{\bullet -}$ and $HO^{\bullet}$ with α,α,α-trifluorotoluene and 4-fluorotoluene were obtained by flash photolysis.

The photolysis of strong alkaline solutions (pH > 12.7) of hydrogen peroxide ($pK_a = 11.6$[1]) yields $HO^{\bullet}/O^{\bullet -}$ radicals ($pK_a \approx 11.9$) [eqns. (1) and (−1) in Table 1]. In the presence of molecular oxygen, $O^{\bullet -}$ radicals reversibly react with O_2 yielding ozonide radical ions, $O_3^{\bullet -}$ [eqns. (2) and (3)] .[2–4] Ozonide itself is thought to be rather unreactive towards non-radical substrates; however its decay rate is extremely sensitive to small quantities of $HO^{\bullet}/O^{\bullet -}$ scavengers.[5–7] In previous investigations[4] it has been shown that in solutions containing H_2O_2 concentrations of the order of 5×10^{-5} mol dm^{-3} or larger and added substrates (S), competition between H_2O_2, S and O_2 for $O^{\bullet -}/HO^{\bullet}$ radicals rules the formation efficiency and decay rate of $O_3^{\bullet -}$. A detailed kinetic study on the $O_3^{\bullet -}$ concentration profiles following flash photolysis of alkaline hydrogen peroxide solutions in the presence of scavengers yields kinetic information on the reactions between $O^{\bullet -}/HO^{\bullet}$ and the substrates [eqns. (6) and (7)].[4] Based on this methodology, we report here a kinetic study of the reactions of $O^{\bullet -}/HO^{\bullet}$ radicals with α,α,α-trifluorotoluene (TFT) and 4-fluorotoluene (4-FT).

Experimental

Hydrogen peroxide (Riedel-de Haën), TFT and 4-FT (Fluka) were used as received. The flash-photolysis set-up and experimental procedures are described elsewhere.[4]

All the experiments were carried out at 25 ± 1 °C. In order to study the effect of substrates on the $O_3^{\bullet -}$ decay kinetics, a series of experiments with 1.16×10^{-4} mol dm^{-3} hydrogen peroxide and systematic variations in the amounts of substrate ($0–4 \times 10^{-3}$ mol dm^{-3}) and pH were performed.

Results and Discussion

The time-resolved absorption curves obtained in the range 350–700 nm show the presence of a single intermediate identified as $O_3^{\bullet -}$ by its characteristic absorption spectrum.[4] The traces can be well described by a first-order law over more than three lifetimes under all the experimental conditions (Fig. 1). The observed rate constant, k_{app}, linearly depends on the analytical concentration of added substrate at constant pH as shown in Fig. 2 (inset).

Table 1 Manifold of important reactions leading to the formation and decay of ozonide radical ions in the presence of efficient $O^{\bullet -}/HO^{\bullet}$ radical scavengers[a]

Reaction	k/dm^3 mol^{-1} s^{-1}	
$HO^{\bullet} + HO^{-} \rightarrow O^{\bullet -}$	1.3×10^{10}	(1)
$O^{\bullet -} + H_2O \rightarrow HO^{\bullet} + HO^{-}$	1.8×10^{6}	(−1)
$O^{\bullet -} + O_2 \rightarrow O_3^{\bullet -}$	3.6×10^{9}	(2)
$O_3^{\bullet -} \rightarrow O^{\bullet -} + O_2$	$3.6–6.0 \times 10^{3}$ s^{-1}[b]	(3)
$HO^{\bullet} + HO_2^{-} \rightarrow O_2^{\bullet -} + H_2O$	9.0×10^{9}	(4)
$O^{\bullet -} + HO_2^{-} \rightarrow O_2^{\bullet -} + HO^{-}$	5.0×10^{8}	(5)
$O^{\bullet -} + S \rightarrow$ Products		(6)
$OH^{\bullet} + S \rightarrow$ Products		(7)

[a] Taken from refs. 5, 9 and 11. [b] The value 4.0×10^{3} s^{-1} was used at 25 °C, in line with the reported value for the activation energy of this reaction (46 kJ mol^{-1}).[12]

Previous investigations on the photolysis of alkaline solutions of hydrogen peroxide, have shown that reactions (1)–(5) in Table 1 are the main reactions leading to ozonide formation and decay.[4] If organic substrates such as 4-FT and TFT are added, they will also contribute to the depletion of $O^{\bullet -}/HO^{\bullet}$ according to reactions (6) and (7).

Any possible reaction of $O^{\bullet -}/HO^{\bullet}$ and $O_3^{\bullet -}$ with the radical products, $S^{\bullet}$, formed from eqns. (6) and (7) should also be considered. The total amount of $S^{\bullet}$ formed can be estimated from the ratio of the areas of the ozonide decay profiles in the presence and absence of scavenger, respectively. For experiments with the highest concentrations of scavenger, $[S^{\bullet}]_{total} \ll 8 \times 10^{-7}$ mol dm^{-3}. Consequently, $S^{\bullet}$ cannot compete for $O^{\bullet -}/HO^{\bullet}$ radicals with the efficient scavenging by much larger concentrations of H_2O_2 and substrates, and eqn. (8) is negligible under our experimental conditions. However, the contribution of the reaction of $S^{\bullet}$ with $O_3^{\bullet -}$ [eqn. (9)] cannot be evaluated *a priori* without a complete kinetic analysis. In a simplified analysis, reaction (9) will not be considered.

$$O^{\bullet -}/HO^{\bullet} + S^{\bullet} \rightarrow \text{Products} \tag{8}$$

$$O_3^{\bullet -} + S^{\bullet} \rightarrow \text{Products} \tag{9}$$

The reaction mechanism shown in Table 1 can be analytically resolved assuming steady-state conditions for the extremely reactive $O^{\bullet -}$ and $HO^{\bullet}$ radicals. From this kinetic analysis, a first-order law is expected for the decay of ozonide radical ions.[4] The first-order apparent rate constant k_{app} is given by eqn. (10). A more detailed discussion on the reaction mechanism and kinetic analysis can be found in the literature.[4]

$$k_{app} = \frac{k_3\{k'[HO_2^-] + k_s[S]\}}{k_2[O_2] + k'[HO_2^-] + k_s[S]} \tag{10}$$

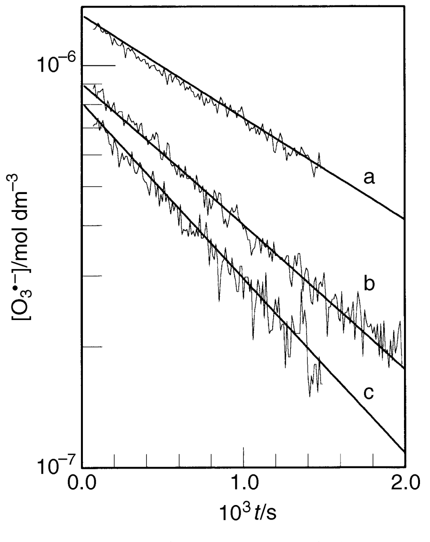

Fig. 1 Logarithmic plots for the decay of $[O_3^{\bullet -}]$ obtained for air-saturated alkaline 1.16×10^{-4} mol dm^{-3} H_2O_2 solutions (pH = 13.9) containing (a) no added scavengers, (b) 3.87×10^{-5} mol dm^{-3} 4-FT and (c) 1.61×10^{-3} mol dm^{-3} TFT: solid lines represent computer simulations of the decays (see text)

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡*E-mail*: dmartire@volta.ing.unlp.edu.ar.

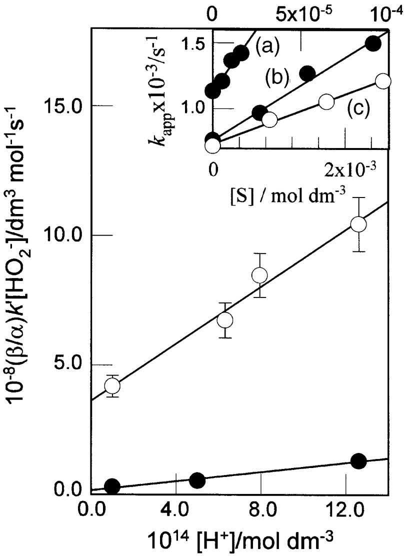

Fig. 2 Plots of $(\beta/\alpha) \times [HO_2^-]k'$ *vs*. $[H^+]$ for (●) TFT and (○) 4-FT: the error in each data point was estimated from the dispersion in the calculated values of α and β. For 4-FT, the error bars are of the same size as the symbols. *Inset*: Plots of k_{app} *vs.* [S] for air-saturated alkaline solutions containing 1.16×10^{-4} mol dm^{-3} H_2O_2 and (a) TFT, pH = 12.9; (b) TFT, pH = 13.3; (c) 4-FT, pH = 12.9 (upper *x* axis)

with

$$k_s = k_6 + k_7K^{-1}[H^+]$$
$$k' = k_5 + k_4[H^+]/K$$
$$K = [O^{\bullet -}][H^+]/[HO^\bullet] = 1.26 \times 10^{-12} \qquad (11)$$

If $k_2[O_2] + k'[HO_2^-] >> k_s[S]$, then the linear dependence of k_{app} on [S] is expected as observed experimentally. The ratio of the slope (β) to the intercept (α) of the plots of k_{app} *vs.* [S] (Fig. 2), times $[HO_2^-] \times k'$ yields k_s at a given pH. According to eqn. (11), k_s should linearly depend on $[H^+]$ as experimentally observed (Fig. 2). A least-squares analysis of the plots shown in Fig. 2 allows determination of k_6 and k_7 for each substrate from the intercept and slope, respectively. The values $k_6 = (4 \pm 2) \times 10^8$ dm^{-3} mol^{-1} s^{-1}, $k_7 = (6 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1} and $k_6 = (2 \pm 1) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_7 = (1.1 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1} are retrieved for 4-FT and TFT, respectively. The errors in the rate constants were estimated from the dispersions observed for the intercepts and the slopes in Fig. 2.

In order to support the simplified kinetic analysis, other literature reactions involving the species present in the irradiated system,[4] and not shown in Table 1, were considered in a kinetic simulation program together with reactions (6) and (7). An excellent agreement between experimental and simulated data was obtained for the observed kinetics of $O_3^{\bullet -}$, also shown in Fig. 1, using the values of k_6 and k_7 retrieved from the simplified analysis. Thus, the contribution of reactions other than those shown in Table 1 is negligible under our experimental conditions.

Reaction (9) between $O_3^{\bullet -}$ and the $S^\bullet$ radicals was not considered in a first approximation, though its participation in the overall mechanism is expected to accelerate the decay kinetics of ozonide radical ions. Consequently, the retrieved values of k_6 and k_7 are upper limits for these rate constants. The contribution of this reaction to the concentration profiles of $O_3^{\bullet -}$ in the presence of added S was evaluated with the aid of the computer simulation program. The simulations show that taking $k_9 = 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, and in the extreme conditions where no other decay reaction for $S^\bullet$ is considered, the values of k_6 and k_7 that best fit the experimental ozonide profiles are 50% lower than those estimated without considering eqn. (9). There is almost no contribution from this reaction to the ozonide decay if $k_9 \leq 5 \times 10^8$ dm^3 mol^{-1} s^{-1}.

The reactions of substituted benzenes with $O^{\bullet -}/HO^\bullet$ are known to yield reactive hydroxycyclohexadienyl and/or benzyl radicals.[8] Consequently, $S^\bullet$ may undergo other reactions in competition with reaction (9), and the effect of the latter reaction on the estimated values of k_6 and k_7 will be much lower than 50%. Thus, any possible effect of reaction (9) is already included within the reported error bars for k_6 and k_7, even in the case that eqn. (9) is diffusion-controlled.

The rate constant obtained for the reaction of $HO^\bullet$ and TFT is lower than the reported ones for toluene [$(3–7) \times 10^9$ dm^3 mol^{-1} s^{-1}] and benzene (5.0×10^9 dm^3 mol^{-1} s^{-1}), and similar to that for nitrobenzene (2×10^9 dm^3 mol^{-1} s^{-1}).[9] This trend is expected from a radical addition of $HO^\bullet$ to the aromatic ring, considering the electron-withdrawing ability of the CF_3 group. On the other hand, the rate constant for the reaction of 4FT and $HO^\bullet$ is of the same order as the reported values for other toluenes with *para* electron-withdrawing substituents (*i.e.* 7×10^9, 2.9×10^9 and 5.5×10^9 dm^3 mol^{-1} s^{-1} for *p*-nitrotoluene, *p*-bromotoluene and *p*-chlorotoluene, respectively).[9,10] The rate constant obtained for the reaction of $O^{\bullet -}$ and TFT is two orders of magnitude smaller than that observed for toluene (2.1×10^9 dm^3 mol^{-1} s^{-1}), but of the same order of magnitude than the reported ones for benzene (7.5×10^7 dm^3 mol^{-1} s^{-1}), benzonitrile (7×10^7 dm^3 mol^{-1} s^{-1}) and nitrobenzene (5×10^7 dm^3 mol^{-1} s^{-1}). The higher reactivity of $O^{\bullet -}$ with toluene indicates the preferential reaction of this radical by H abstraction from aliphatic side chains of the aromatic molecules, rather than by addition to the aromatic ring.[9] On the other hand, the rate constant obtained for the reaction of $O^{\bullet -}$ and 4-FT is of the same order as the reproted values for other toluenes containing electron-withdrawing substituents, such as nitrotoluene (7.6×10^8 dm^3 mol^{-1} s^{-1}).[9]

M. C. G. and D. O. M. are research members of CONICET and CICPBA, respectively. This research was partially supported by grants number A-13218/1-000062 and A-13359/1-000084 of Fundación Antorchas (Argentina)

Received, 6th January 1997; Accepted, 4th February 1997
Paper E/7/00126F

References

1 K. Chelkowska, D. Grasso, I. Fábián and G. Gordon, *Ozone Sci. Eng.*, 1992, **14**, 33.
2 J. Hunt and H. Taube, *J. Am. Chem. Soc.*, 1952, **74**, 5999.
3 J. H. Baxendale and J. A. Wilson, *Trans. Faraday Soc.*, 1957, **53**, 344.
4 M. C. Gonzalez and D. O. Mártire, *Int. J. Chem. Kin.*, in press.
5 K. Sehested, J. Holcman, E. Bjerbakke and E. J. Hart, *J. Phys. Chem.*, 1982, **86**, 2066.
6 B. L. Gall and L. M. Dorfman, *J. Am. Chem. Soc.*, 1969, **91**, 2199.
7 G. Czapski, *Annu. Rev. Phys. Chem.*, 1971, **22**, 171.
8 (*a*) C. von Sonntag and H.-P. Schuchmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1229; (*b*) P. Neta, J. Grodkowski and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1996, **25**, 709.
9 (*a*) G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513; (*b*) Farhataziz and A. B. Ross, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solutions. II. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions*, NSRDS-NBS 59, National Bureau of Standards, Washington DC, 1977.
10 G. Merga, B. S. M. Rao, H. Mohan and J. P. Mittal, *J. Phys. Chem.*, 1994, **98**, 9158.
11 P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027.
12 D. Behar, *J. Phys. Chem.*, 1974, **78**, 2660.