Halogenated Peroxyl Radicals as Multi-Electron Oxidants: Pulse Radiolysis Study on the Reaction of Trichloromethyl Peroxyl Radicals with Iodide

Marija Bonifačić,*[a] Christian Schöneich[b] and Klaus-Dieter Asmus*[b]

[a] *Ruđer Bošković Institute, Department of Physical Chemistry, PO Box 1016, 41001 Zagreb, Croatia, Yugoslavia*
[b] *Hahn-Meitner-Institute Berlin, Bereich S, Abteilung Strahlenchemie, Postfach 39 01 28, 1000 Berlin 39, Germany*

$CCl_3OO^•$ radicals are shown to oxidize three equivalents of iodide ions to yield one I_2 molecule (showing up as I_3^- in aqueous solution) and one $I^•$ atom (showing up as $I_2^{•-}$) per peroxyl unit; the mechanism is considered to proceed *via* a protonated $CCl_3OO^•/I^-$ adduct radical as the primary intermediate and subsequent nucleophilic (S_N2) attack by a second iodide accompanied by electron localization in the hydroperoxide moiety leads to I_2 and $CCl_3O^•$ with the latter being responsible for the oxidation of the third iodide.

In a recent paper we reported on a first example on oxidation reactions by halogenated peroxyl radicals which involve an overall two-electron transfer, namely the oxidation of organic sulphides to sulphoxides in aqueous solutions.[1] An important feature of this process is considered to be a transient peroxyl radical adduct to the sulphide molecule.

In this communication we now present a first example of a quantitative, overall three-electron oxidation of an inorganic substrate by a halogenated peroxyl radical, namely the reaction of trichloromethyl peroxyl radicals with iodide.

Experiments were performed by using the radiation chemical technique of pulse radiolysis. $CCl_3OO^•$ radicals were generated by subjecting air-saturated, pH 4, water–propan-2-ol (70 : 30, v/v) mixtures containing 3×10^{-2} mol dm^{-3} CCl_4 to short pulses of 1.5 MeV electrons from a Van de Graaff accelerator (≈1 μs duration; ≈1.5 Gy [J kg^{-1}] dose).[2,3] The yield of $CCl_3OO^•$ radicals in such systems amounts to $\approx 10^{-6}$ mol dm^{-3} per pulse or, in radiation chemical terms, $G \approx 6.0$ (±0.3) (species per 100 eV absorbed energy).[4,5]

The formation of $CCl_3OO^•$ occurs within the duration of the pulse and is accompanied by liberation of one H^+/Cl^- ion pair as evidenced by an observable step-function type increase in conductivity in time-resolved experiments.[6,7] When iodide (10^{-3} mol dm^{-3}) is added the conductivity signal, as shown in Fig. 1(*a*), still exhibits the H^+/Cl^- formation as the initial step but then decreases by about twice the amount of the initial positive signal to a stable net negative value, indicating the

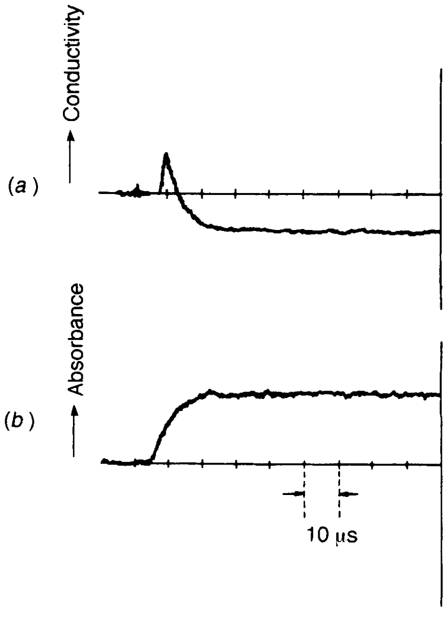


Fig. 1 Conductivity (*a*) and optical absorption at 360 nm (*b*) *vs.* time traces obtained upon pulse radiolysis of air-saturated, water–propan-2-ol (70 : 30, v/v) mixtures containing 3×10^{-2} mol dm^{-3} CCl_4 and 1×10^{-3} mol dm^{-3} KI at pH 4.0

loss of two equivalents each of protons and anions. This decrease in conductivity coincides with the formation of an *optical absorption* as can be seen from the optical trace monitored at 360 nm and displayed in Fig. 1(*b*).

The entire optical absorption spectrum, as recorded 20 μs after the pulse for the 300–800 nm range, is documented in the data point curve (*a*) of Fig. 2. It exhibits a strong UV and a smaller IR band with maxima at 360 and around 720 nm, respectively. The spectral characteristics of the IR band are indicative for $I_2^{\bullet -}$, formally the one-electron oxidation product of iodide. Taking the known extinction coefficient of $I_2^{\bullet -}$ (ε^{750} = 2700 dm^3 mol^{-1} cm^{-1})[8] the yield of the species is calculated to G = 6.0 (±0.3), which equals the yield of available $CCl_3OO^{\bullet}$ radicals. On this basis and considering the known spectral characteristics of the $I_2^{\bullet -}$ absorption in the UV (λ_{max} at 380 nm, ε^{380} = 9400 dm^3 mol^{-1} cm^{-1})[8] it is possible to evaluate the entire $I_2^{\bullet -}$ absorption. This is displayed in the dashed curve (*b*) of Fig. 2.

The differential spectrum [solid curve without data points, (*c*)] shows only one maximum at 360 nm and is characteristic of I_3^- ions.[9] Taking K = 1.4 × 10^3 dm^3 mol^{-1} for the equilibrium $I^- + I_2 \rightleftarrows I_3^-$ and the extinction coefficient ε^{360} = 29 000 dm^3 mol^{-1} cm^{-1} (both obtained from spectral measurements with known amounts of I_2 at different I^- concentrations in 70 : 30 v/v water–propan-2-ol mixtures) the yield of I_3^- is calculated as G = 6.2. This means that any one $CCl_3OO^{\bullet}$ radical, besides generating one equivalent of $I_2^{\bullet -}$, is also responsible for the simultaneous formation of one equivalent of I_3^- which requires two I^- to be oxidized. The formation of I_3^- has been confirmed by spectrophotometrical analysis of corresponding steady-state γ-radiolysis experiments. The measured yield of $G(I_3^-)$ = 8 is in reasonably good agreement with the theoretically possible maximum yield (G = 9).

The formation kinetics of the optical absorptions are of pseudo-first-order with respect to iodide concentration at any pH and wavelength. From measurements at 360 nm and pH 3 a bimolecular rate constant of k = 2.0 × 10^8 dm^3 mol^{-1} s^{-1} has been evaluated. At higher pH this rate constant decreases as shown in Fig. 3. The sigmoidal curve exhibits a break point at pH 4 and attains its lower level (k = 4.0 × 10^7 dm^3 mol^{-1} s^{-1}) at pH ⩾ 6. Measurements at 720 nm exhibit the same dependences on [I^-] and pH. A common rate determining step is thus inferred for the generation of $I_2^{\bullet -}$ and I_3^-.

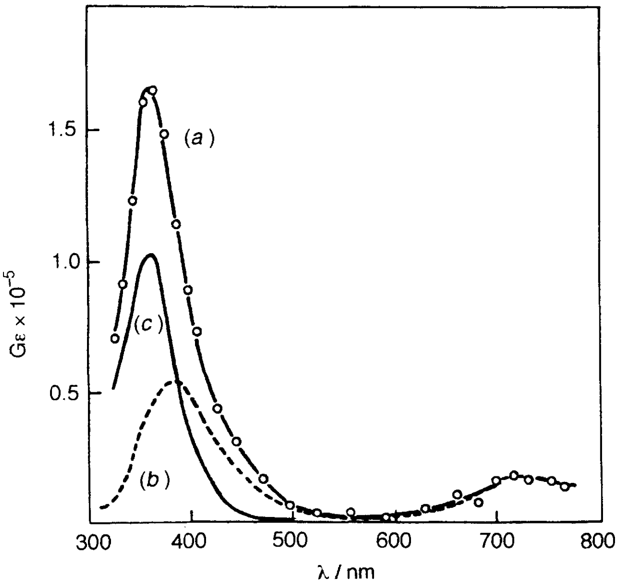
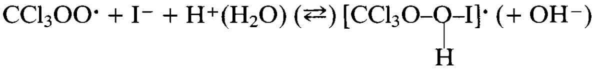


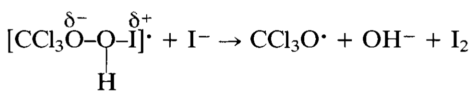
Fig. 2 Optical absorption spectrum recorded *ca.* 20 μs after application of a *ca.* 1 μs pulse to air-saturated, water–propan-2-ol (70 : 30, v/v) mixtures containing 3 × 10^{-2} mol dm^{-3} CCl_4 and 1 × 10^{-3} mol dm^{-3} KI at pH 4.0. Curve (*a*); calculated $I_2^{\bullet -}$ spectrum in same system (*b*); and differential spectrum (*c*) (representing I_3^-) obtained by subtraction of (*b*) from (*a*).

A corresponding [I^-] and pH dependence is also observed for the decay kinetics of the conductivity signal [Fig. 1(*a*)] which parallels the formation of the optical absorptions (over the experimentally accessible pH 3–5.5 range). It is important to recognize that the total yield of conductivity change, *i.e.* the level of the initial increase and final negative signal, remains, however, invariant within this pH range. Finally, it must be noted that the optically determined initial $I_2^{\bullet -}$ and I_3^- yields do not change within the experimentally covered pH 2–10 range.

The following reaction mechanism accommodates all experimental observations; see eqns. (1)–(5). The first step is



$$\mathrm{CCl_3OO^{\bullet} + I^- + H^+(H_2O)\ (\rightleftarrows)\ [CCl_3O{-}\underset{\displaystyle H}{\underset{|}{O}}{-}I]^{\bullet}\ (+\ OH^-)} \qquad (1)$$



$$\mathrm{[CCl_3\overset{\delta-}{O}{-}\underset{\displaystyle H}{\underset{|}{O}}{-}\overset{\delta+}{I}]^{\bullet} + I^- \rightarrow CCl_3O^{\bullet} + OH^- + I_2} \qquad (2)$$

$$\mathrm{CCl_3O^{\bullet} + I^- \rightarrow I^{\bullet} + CCl_3O^- \ (CCl_2O + Cl^-)} \qquad (3)$$

$$\mathrm{I^{\bullet} + I^- \rightleftarrows I_2^{\bullet -}} \qquad (4)$$

$$\mathrm{I_2 + I^- \rightleftarrows I_3^-} \qquad (5)$$

considered to be addition of the peroxyl radical to iodide, concurrent with protonation, to yield the neutral adduct radical. (There is, however, no experimental evidence for a distinct life-time of this species). Nucleophilic (S_N2) attack by a second iodide ion at the probably slightly positive iodine atom in the adduct associated with a Fenton-type electron transfer into the hydroperoxide moiety would then result directly in the generation of I_2 and a $CCl_3O^{\bullet}$ radical. The latter is responsible for the oxidation of the third iodide ion to yield an $I^{\bullet}$ atom *via* eqn. (3).† Complexation of $I^{\bullet}$ and I_2 by an excess of iodide constitutes the ultimate steps *en route* to $I_2^{\bullet -}$ and I_3^-.

Although eqns. (1) and (2) probably do not represent two strictly separable steps it should be recognized that the kinetics of the $I_2^{\bullet -}/I_3^-$ formation could not be influenced by the ionic strength at any investigated pH. This lack of kinetic salt effect would imply that the approach of the second iodide is not hampered by a full negative charge at the primary adduct radical. At the same time it eliminates the possbility of the turning point in Fig. 3 being simply due to an acid–base equilibrium of the adduct radical. Whether reaction (1) may be formulated as an equilibrium cannot be decided on the basis of our experiments; true reversibility may well be hampered by electron delocalization within the adduct radical.

The participation of protons in reaction (1) and possibly also in reaction (2) (assisting the process by neutralization of the hydoxyl ions) plausibly explains the pH dependence of the $I_2^{\bullet -}/I_3^-$ formation kinetics. Optimum conditions in this respect prevail at low pH where sufficiently high concentra-

---

† It is assumed that $CCl_3O^{\bullet}$ oxidizes I^- prior to possible chlorine atom cleavage. Free $Cl^{\bullet}$ atoms would preferentially react with propan-2-ol ($k \approx$ 1 × 10^9 dm^3 mol^{-1} s^{-1})[10] rather than with I^- in our system and hence initiate a chain process which is, however, not observed. Direct reaction of $CCl_3O^{\bullet}$ with propan-2-ol is not considered since it would probably occur too slowly[11] to compete with reaction (3) (estimated by extrapolation from k = 3.7 × 10^9 dm^3 mol^{-1} s^{-1} for the reaction $CH_3O^{\bullet} + I^-$).[11] A possible hypoiodide, HIO, as a free intermediate from the decay of the neutral adduct radical is discarded because the documented kinetics[12] of the necessary follow-up reaction HIO + I^- + $H^+/H_2O \rightarrow I_2 + H_2O/OH^-$ are in conflict with the kinetics measured in this study. The secondary yield of I_3^- owing to disproportion of $I_2^{\bullet -}$ ($2I_2^{\bullet -} \rightarrow I_3^- + I^-$) shows up only at longer times beyond the time scale of Fig. 1.

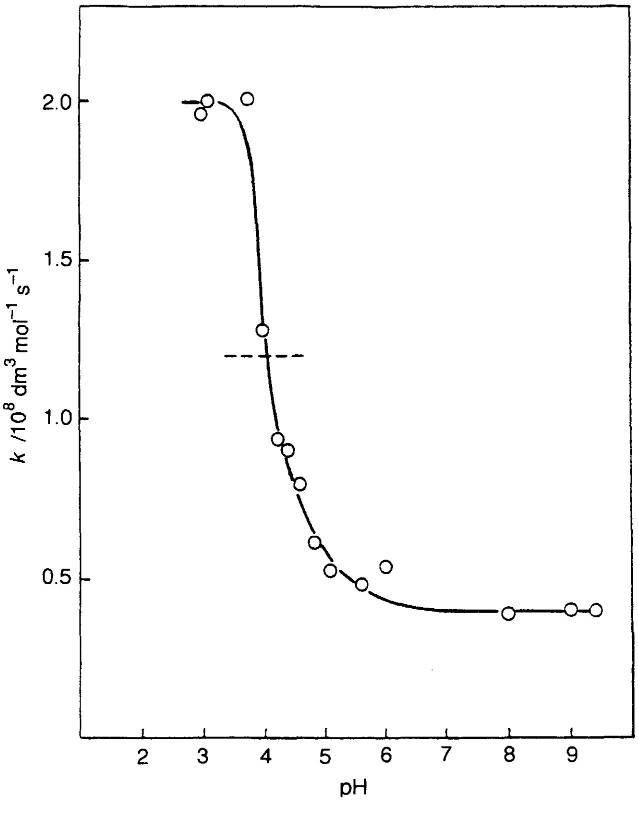


Fig. 3 Second-order rate constants for I_3^- and $I_2^{\bullet -}$ formation *vs.* pH. Conditions as in Fig. 1.

tions of free protons are available. At higher pH the protons have to be taken from the surrounding water molecules, a process which is thermodynamically less favourable and therefore occurs at lower rate.

The conductivity changes associated with the $I_2^{\bullet -}/I_3^-$ formation accounted for by the conversion of two iodide ions [eqns. (1) and (2)] into the netural I_2, and the consumption of two protons in neutralization reactions with OH^-.

The results reported in the present communication on the $CCl_3OO^\bullet$ induced oxidation of iodide resemble certain features of the $O_2(^1\Delta)$ induced oxidation of I^- to I_2,[13] and in a quantitative manner fully corroborate our earlier finding on the $R(Hal)OO^\bullet$ induced oxidation of organic sulphides to sulphoxides.[1] We feel that our results now allow to generalize the multi-electron redox capacity of halogenated peroxyl radicals.

Received, 29th April 1991; Com. 1/02003J

References

1 Ch. Schöneich, A. Aced and K.-D. Asmus, *J. Am. Chem. Soc.*, 1991, **113**, 375.
2 K.-D. Asmus, in *Methods in Enzymology*, ed. L. Packer, Academic Press, Orlando, 1984, vol. 105, pp. 167.
3 J. Mönig, M. Göbl and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1985, 647.
4 X. Chen, J. Lind, T. E. Eriksen and G. Merényi, *J. Phys. Chem.*, 1989, **93**, 553.
5 C. v. Sonntag, *The Chemical Basis of Radiation Biology*, Taylor & Francis, London, 1987.
6 R. Köster and K.-D. Asmus, *Z. Naturforsch. Teil B*, 1971, **26**, 1104.
7 K.-D. Asmus and E. Janata, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, eds. J. H. Baxendale and F. Busi, NATO-ASI Series C, Reidel Publ. Co., Dordrecht, 1982, vol. 86, pp. 91.
8 G. L. Hug, *Nat. Stand. Ref. Data Ser.*, US Dept. of Commerce, Washington D.C., 1981, vol. 69.
9 A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, 1951, **73**, 1842.
10 B. C. Gilbert, J. K. Stell, W. J. Peet and K. J. Radford, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3319.
11 D. H. Ellison, G. A. Salmon and F. Wilkinson, *Proc. R. Soc. Lond. A*, 1972, **328**, 23.
12 M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, 1962, **84**, 1355; O. Citri and I. R. Epstein, *J. Phys. Chem.*, 1987, **91**, 6034.
13 G. Braathen, P.-T. Chou and H. Frei, *J. Phys. Chem.*, 1988, **92**, 6610.