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OXIDATION OF ORGANOPHOSPHORUS COMPOUNDS—IV[1]

KINETICS AND MECHANISM OF THE OXIDATION OF DIARYLPHOSPHINE OXIDES BY *t*-BUTYL HYDROPEROXIDE, HYDROGEN PEROXIDE AND *p*-NITROPEROXYBENZOIC ACID IN ALKALINE MEDIA

R. CURCI and F. DI FURIA

Istituto di Chimica Organica dell 'Universita', Centro di Meccanismi
di Reazioni Organiche del C.N.R., 35100 Padova, Italy

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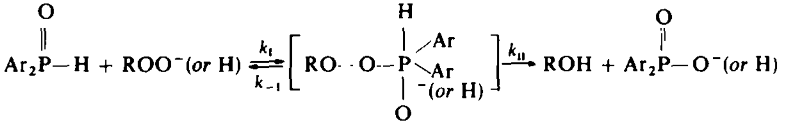
Abstract—The influence of OH^- concentration, in the solvent medium dioxane-water 40:60 at 25·0, on the oxidation rates of diphenylphosphine oxide (DPPO) by *t*-BuOOH, H_2O_2 and *p*-nitroperoxybenzoic acid, and of bis-*p*-tolylphosphine oxide by *t*-BuOOH has been investigated. For the oxidation of the phosphorus substrates by the hydroperoxides above, the rate law found ($R = k_2''[Ar_2PHO][ROO^-]$) differs from the rate law confirmed to hold for the oxidation of DPPO by peroxyacids in alkaline media, *i.e.*: $R = (k_2'' + k_3[OH^-])[Ar_2PHO][RCO_3^-]$. This is interpreted on the basis of one common reaction mechanism involving formation of an intermediate of similar structure, wherein a change in the rate controlling step is likely to occur on passing from $p\text{-}O_2N\cdot C_6H_4CO_3^-$ to *t*-$BuOO^-$. In the same solvent medium, pK_a' values for t-BuOOH and H_2O_2 have been estimated.

IN PREVIOUS studies[1-3] kinetic evidence has been presented which suggests the oxidation of secondary phosphine oxides **1** to the corresponding phosphinic acids **4** by peroxybenzoic acid [in **2**, R = PhC(:O)—], both in acidic and alkaline media, occurs by means of preliminary nucleophilic attack of the peroxidic species on the organophosphorus substrate. This would lead to a reactive intermediate **3** which in turn would decompose to give the observed reaction products:



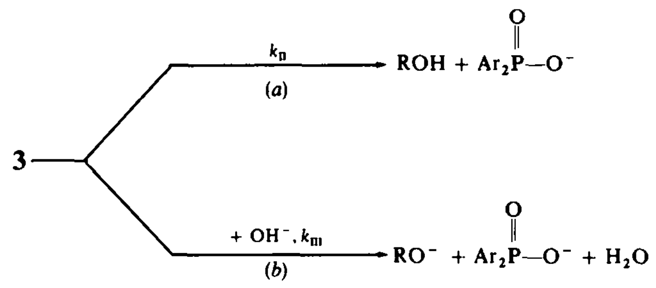
$$Ar_2\overset{\overset{\displaystyle O}{\|}}{P}-H + ROO^-(or\ H) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[RO-O-\underset{\underset{\displaystyle O}{|}}{\overset{\overset{\displaystyle H}{|}}{P}}\begin{matrix}\diagup Ar\\ \diagdown Ar\end{matrix}\ ^-(or\ H)\right] \xrightarrow{k_{II}} ROH + Ar_2\overset{\overset{\displaystyle O}{\|}}{P}-O^-(or\ H) \qquad (1)$$

1 **2** **3** **4**

In dioxan-water 40:60, the following general rate law was found to hold:

$$R = (k_2'[PhCO_3H] + k_2''[PhCO_4^-] + k_3[PhCO_3^-][OH^-])[Ar_2PHO] \qquad (2)$$

According to Eq. (2), for solutions of relatively high OH^- concentration (i.e., apparent pH > 13), where the peroxyacid (apparent $pK_a \backsim 9$) is present almost entirely in its anion form $PhCO_3^-$, the observed second-order rate constant was found to be linearly dependent on $[OH^-]$. Thus, it became apparent that, in markedly alkaline media, a competitive pathway is available for decomposition of intermediate **3**:



(3)

[with R = PhC(:O)−]

Given the general rate law observed, on the basis of a steady-state treatment for the mechanism expressed by Eqs (1) and (3), we suggested that, for the oxidation of secondary phosphine oxides by peroxybenzoic acid (PBA), the formation of the reactive intermediate **3** is faster than its decomposition. A subsequent study on the kinetic deuterium isotope effects also supported this view.[1]

Since it is known that the oxidation of many organic and inorganic substrates by hydroperoxides and hydroperoxide anions often occurs according to a two-step mechanism,[4–6] we decided to undertake an investigation on the kinetics of oxidation of secondary diarylphosphine oxides by hydrogen peroxide, t-butyl hydroperoxide and by *p*-nitroperoxybenzoic acid. Our aim was to check on the general validity of the mechanism presented in Eq. (1) as well as to gain further insights into the balance of this interesting two-step redox process.

RESULTS

Oxidation by p-*nitroperoxybenzoate anion*

The oxidation reaction of diphenylphospine oxide (DPPO) by *p*-nitroperoxybenzoic acid, in dioxan–water 40:60 at 25·0°, showed the same kinetic features already observed for the oxidation of the same substrate by PBA.[1,2] At such alkalinity levels of the reaction solvent as to ensure that *p*-nitroperoxybenzoic acid (pK_a 7·29 in water, at 25·0°) is predominantly present as its parent anion $p\text{-}O_2N\cdot C_6H_4CO_3^-$, it was again found that $k_2(\mathrm{obs})$ values correlate linearly with OH^- concentration. Kinetic data are summarized in Table 1; on plotting $k_2(\mathrm{obs})$ values *vs* $[OH^-]$ a straight line was obtained (corr. coeff. 0·998). According to the equation[1,2] $k_2(\mathrm{obs}) = k_2'' + k_3[OH^-]$, from the intercept and the slope of such plot k_2'' and k_3 values could be estimated: these are 0·11 $M^{-1}\,\mathrm{sec}^{-1}$ and 7·52 $M^{-2}\,\mathrm{sec}^{-1}$ respectively.

Oxidation by t-butyl hydroperoxide and by hydrogen peroxide anions

Rate data for the oxidation of DPPO by hydrogen peroxide and by t-butyl hydroperoxide, in dioxan–water 40:60 at 25·0°, at various apparent pH or H_- values are given in Table 2. On the same table are also shown rate data concerning the oxidation of bis-*p*-tolylphosphine oxide by t-BuOOH.

In agreement with what was previously observed in the oxidation of diarylphosphine oxides by PBA at various pH_{app} values,[2] in all instances the kinetics were found to obey a second-order-overall (order one in each of the reagents) kinetic law up to

TABLE 1. RATES OF OXIDATION OF DIPHENYLPHOSPHINE OXIDE BY p-NITROPEROXYBENZOATE ANION IN DIOXAN-WATER 40:60, TEMPERATURE 25·0°[a]

H_-[b]	13·56	13·78	14·06	14·16	14·40
OH^-, M	0·030	0·050	0·095	0·120	0·210
k_2(obs), M^{-1} sec^{-1}	0·386	0·443	0·800	1·02	1·70

[a] Reactants concentrations were kept in the range 0·008–0·012 M.

[b] As measured using the method described by R. Stewart and J. P. O'Donnell (Experimental).

TABLE 2. OXIDATION RATES OF DIPHENYLPHOSPHINE OXIDE BY HYDROGEN PEROXIDE (REACTION A) AND BY t-BUTYL HYDROPEROXIDE (REACTION B), AND OXIDATION RATES OF BIS-p-TOLYLPHOSPHINE OXIDE BY t-BUTYL HYDROPEROXIDE (REACTION C) IN DIOXAN-WATER 40:60, TEMPERATURE 25·0°[a]

[b]pH_{app}	[c]H_-	10^2k_2(obs), M^{-1}sec^{-1}		
		Reaction A	Reaction B	Reaction C
7·60		slow[d]	slow[d]	slow[d]
11·00		0·532	—	—
11·05		—	0·137	—
11·10		0·200	—	—
11·30		0·370	0·180	—
11·60		—	0·550	—
11·70		—	—	0·100
12·00		—	1·49	—
12·15		—	—	0·270
12·50		8·92	3·70	—
12·80		—	—	2·82
13·00		—	18·3	—
13·62		16·6	37·0	—
13·68		—	—	7·83
13·98		17·7	62·6	—
	14·00	—	68·3	12·03
	14·32	19·2	—	—
	14·35	—	99·5	16·4
	14·52	—	—	21·4
	14·54	—	98·4	—
	14·64	—	101·0	—
	14·68	—	111·0	—
	14·70	20·2	—	—
	15·15	21·6	—	—
		21·4[e]	115·0[e]	24·0[e]

[a] Reactants concentrations were kept in the range 0·005–0·015 M.

[b] As determined by a conventional glass electrode (see Experimental).

[c] As measured using the method described by R. Stewart and J. P. O'Donnell (Experimental).

[d] Reactions are too slow to be conveniently followed (see Results).

[e] k_2'' values.

70–80% reaction or more. It was found that, under the conditions employed in this study, at pH_{app} values lower than ~8 all of the three reactions investigated proceed very slowly; actually, the reaction rate—as followed by measuring the decrease in hydroperoxide concentration with time—compares very nearly with the rate of the slow uncatalyzed self-decomposition reaction of the hydroperoxide alone.[7] As the alkalinity of the solvent is increased, however, the rate was found to increase steadily up to a point where from further changes in the H_- value caused only small variations in the k_2(obs) value.

A plot of log k_2(obs) values *vs* pH_{app} (or H_-) for the three reaction mentioned is shown in Fig 1; noteworthy, in each of the cases an initial slope of *ca* 1·0 can be evaluated. This suggests that the following rate law applies:

$$-(d[P]/dt) = k_2(\text{obs})[Ar_2PHO][P] = k_2'[Ar_2PHO][ROOH] + k_2''[Ar_2PHO][ROO^-] \cong k_2''[Ar_2PHO][ROO^-] \quad (4)$$

where:

$$[P] = [ROOH] + [ROO^-] \quad (5)$$

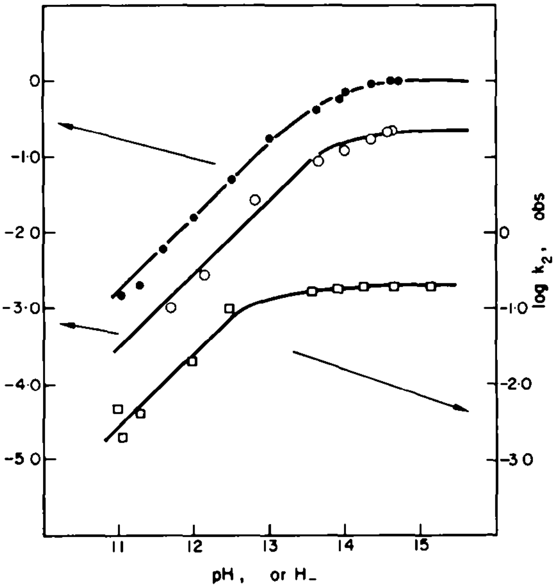
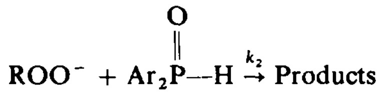


FIG 1. Observed rates as a function of acidity for the oxidation of DPPO by *t*-butyl hydroperoxide (full circles) and by hydrogen peroxide (empty squares), and for the oxidation of bis-*p*-tolyl diphenylphosphine oxide by *t*-butyl hydroperoxide (empty circles).

As a first approximation, therefore, the oxidation process can be defined through the following Eqns:

$$ROOH + OH^- \overset{K_e}{\rightleftarrows} ROO^- + H_2O \quad (6)$$


(7)

$$ROO^- + Ar_2\overset{\overset{\displaystyle O}{\|}}{P}\text{—}H \xrightarrow{k_2} \text{Products} \quad (7)$$

Since it is:

$$([ROO^-]/[ROOH]) = K_e[OH^-] \tag{8}$$

and:

$$([ROO^-]/[P]) = \{K_e[OH^-]/(1 + K_e[OH^-])\} = f \tag{9}$$

it follows that:

$$k_2(\text{obs}) \cong k_2'' \cdot f \tag{10}$$

To verify Eq. (10), it was therefore necessary to evaluate the K_e' values for H_2O_2 and t-BuOOH in the mixed solvent adopted for the kinetic runs. This was achieved by using a known UV spectrophotometric technique[6,7] (Experimental) employing the significant difference in the molar extinction (ε) which is usually found among hydroperoxides and hydroperoxide anions, through the equation:

$$\frac{[ROO^-]}{[ROOH]} = \left(\frac{\varepsilon - \varepsilon_{ROOH}}{\varepsilon_{ROO^-} - \varepsilon}\right) = K_e'[OH^-] \tag{11}$$

The results of these measurements are reported on Fig 2. Both for hydrogen peroxide and t-butyl hydroperoxide, plots of log $([ROO^-]/[ROOH])$ *vs* log $[OH^-]$ were linear with slope close to unity, thus allowing one to estimate log K_e' values from the intercepts; these were 2·21 ± 0·11 for hydrogen peroxide and 1·27 ± 0·05 for t-butyl hydroperoxide.

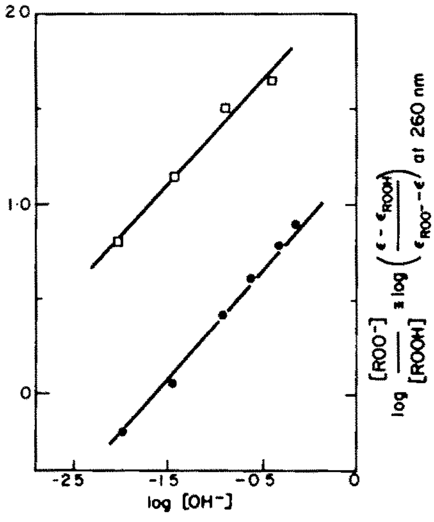


FIG 2. Evaluation of K_e' values for *t*-BuOOH (full circles) and for HOOH (empty squares) in dioxan-water 40:60.

On the basis of a pK_w' value of 15·08 ± 0·10 for the apparent autoprotolysis constant of water in the solvent medium adopted (Experimental), pK_a' values of 12·85 ± 0·15 and 13·80 ± 0·10 can be estimated for H_2O_2 and t-BuOOH respectively.

Having determined the K_e' values for both of the peroxidic species, it was then possible to test the validity of Eq. (10) in accounting for the kinetic data at various pH or H_- values for each of the reactions studied. In fact, Eq. (10) predicts that plots of log k_2(obs) *vs* $\log(K_e[OH^-]/1 + K_e[OH^-])$ should be linear with unit slope. Inspection of Fig 3 reveals that this expectation is satisfactorily fulfilled; the intercepts of these plots gave log k_2'' values, and hence k_2'' values for reactions A, B and C which appear on Table 2 (last entries).

Furthermore, once k_2'' and K_e' values were estimated, it became possible to obtain the calculated log k_2(calc) *vs* pH (or H_-) profiles for each of the three reactions: these are displayed as solid curves on Fig 1.

DISCUSSION

In discussing the mechanisms of the reactions investigated, the first significant aspect to be accounted for is that the rate law obeyed by the reaction of diarylphosphine oxides with hydroperoxides (Eq. 4) seem to differ significantly from the general rate law holding for the oxidation of the same substrates by peroxyacids (Eq. 2).

Particularly, a linear dependence of k_2(obs) values upon OH^- concentration above pH_{app} *ca* 13, which was observed in the oxidation of DPPO by peroxybenzoate and *p*-nitroperoxybenzoate anions, appears to be absent in the reaction of the same substrate with either HOO^- or t-$BuOO^-$.

As already reported in our previous article,[1] using the steady-state approximation for the reactive intermediate 3, one can derive the algebraic expression of k_2(obs)—the overall second-order rate coefficient—for the proposed general reaction mechanism (Eqns 1 and 3):

$$k_2(\mathrm{obs}) = \frac{k_{\mathrm{I}}k_{\mathrm{II}} + k_{\mathrm{I}}k_{\mathrm{III}}[OH^-]}{k_{-\mathrm{I}} + k_{\mathrm{II}} + k_{\mathrm{III}}[OH^-]} \qquad (12)$$

According to Eq. (12), the occurrence and the form of catalysis by OH^- is bound to some specific requirements. This is readily seen when one considers two limiting cases: when $k_{-\mathrm{II}} \gg (k_{\mathrm{II}} + k_{\mathrm{III}}[OH^-])$, Eq. (12) reduces to:

$$k_2(\mathrm{obs}) = (k_{\mathrm{I}}k_{\mathrm{II}}/k_{-\mathrm{I}}) + (k_{\mathrm{I}}k_{\mathrm{III}}/k_{-\mathrm{I}})[OH^-] = k_2'' + k_3[OH^-] \qquad (13)$$

Therefore, assuming the products yielding processes from intermediate 3 (Eq. 3, paths *a* and *b*) are slower than its formation, catalysis by OH^- is expected: this is indeed found in the reaction of DPPO with $C_6H_5CO_3^-$ and with $p\text{-}O_2N\cdot C_6H_4CO_3^-$. On the other hand, when $k_{-\mathrm{I}} \ll k_{\mathrm{II}} + k_{\mathrm{III}}[OH^-]$, Eq. (12) becomes:

$$k_2(\mathrm{obs}) = (k_{\mathrm{I}}k_{\mathrm{II}} + k_{\mathrm{I}}k_{\mathrm{III}}[OH^-])/(k_{\mathrm{II}} + k_{\mathrm{III}}[OH^-]) \qquad (14)$$

Under these circumstances catalysis by OH^- should not be observable: it is likely that these latter requirements are approached in the oxidation of DPPO by HOO^- and by t-$BuOO^-$.

It seems, therefore, that the same general mechanistic scheme can be maintained for the oxidation of diarylphosphine oxides both by peroxyacid anions and by hydroperoxide anions, provided one makes the assumption that changes in $k_{-\mathrm{I}}$ are large when compared to the changes in k_{II} and k_{III}. This is not unreasonable when the

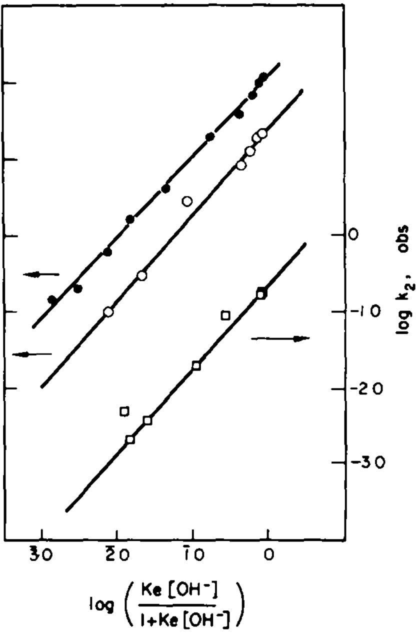


Fig 3. Evaluation of k_2'' values for the oxidation of DPPO by *t*-BOO$^-$ (full circles) and by HOO$^-$ (empty squares), and for the oxidation of bis-*p*-tolylphosphine oxide by *t*-BuOO$^-$ (empty circles).

significant difference in acidity among peroxyacids and hydroperoxides is taken into account.[6]

Comparing now k_2'' values for the oxidation of DPPO and of bis-*p*-tolylphosphine oxide by t-BuOO$^-$ (Table 2), it would be possible to estimate a Hammett ρ value of roughly 1·5. This is about one unit smaller than the ρ value (+2·7) found in the oxidation of substituted diphenylphosphine oxides by peroxybenzoate anion. Such finding is not inconsistent with the view that the intermediate formation step may control the overall kinetics in the oxidation by hydroperoxide anions.

On Table 3 some salient data are summarized which allow comparison of rate data with pK_a's of the peroxidic species as well as with pK_a^{ROH} values, which might be taken as a measure of leaving group ability. The increase in k_3 values observed on passing from peroxybenzoate to *p*-nitroperoxybenzoate anion is relatively small and could be rationalized on the basis of the greater leaving group ability of p-$O_2N{\cdot}C_6H_4CO_2^-$ when compared with $C_6H_5CO_2^-$ (Eq. 3, path *b*).

On the other hand, on plotting log k_2'' *vs* pK_a^{ROH} values, a curved line would result. Non-linear free energy relationship plots (as, e.g., curved Hammett plots)[8] are commonly taken as evidence for the occurrence of a change in the rate controlling step for mechanisms involving intermediate formation. Thus, the observed trend in k_2'' values can also be accommodated within the general mechanism given above, even though it seems unlikely that a complete inversion in the rate determining step occurs on passing from *p*-nitroperoxybenzoate to t-BuOO$^-$. It is worth mentioning that care should be exercised in comparing k_2'' values of the various peroxidic species in Table 3, as they have different algebraic expressions: namely, for the oxidation by

HOO^- and by t-$BuOO^-$ it is (from Eqs 14 and 10):

$$k_2'' = \{(k_I k_{II} + k_I k_{III}[OH^-])/(k_{II} + k_{III}[OH^-])\} \cdot (1/f) \tag{15}$$

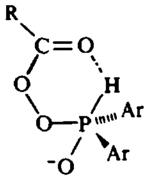
whereas for the oxidation of DPPO by peroxyacid anions k_2'' actually measure the OH^- independent process, being $k_2'' = (k_I k_{II}/k_{-I})$.

Nonetheless, the fact that k_2'' value for the oxidation of DPPO by t-$BuOO^-$ is about ten times as large as in the oxidation of the same substrate by $C_6H_5CO_3^-$ cannot be easily interpreted, unless some special effects are invoked such as, e.g., steric hindrance to solvation of t-$BuOO^-$; or, perhaps, the occurrence of cyclic, internally hydrogen-bonded structures such as **5**, which would lower the relative energy content of the intermediate along the reaction path of DPPO with peroxyacid anions.

TABLE 3. COMPARISON OF OXIDATION RATES OF DIPHENYLPHOSPHINE OXIDE BY SOME PEROXYANIONS IN DIOXAN–WATER 40:60, TEMPERATURE 25.0°

ROO^-	$^a pK_a'^{ROOH}$	$10^2 k_2''^{\,b}$	$10^2 k_3^{\,c}$	pK_a^{ROH}
$(p)O_2N \cdot C_6H_4CO_3^-$	(8·0–8·2)	11·0	752·0	3·41
$PhCO_3^-$	8·8–9·0	10·4	223·0	4·19
HOO^-	12·85	21·4	—	15·75[d]
t-$BuOO^-$	13·80	115·0	—	(20·0)

[a] Apparent pK_a values in the mixed solvent adopted.
[b] in $M^{-1}sec^{-1}$.
[c] in $M^{-2}sec^{-1}$.
[d] from: M. Eigen, *Angew. Chem.* Inter. Ed. 3, 1 (1964).



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As already pointed out,[1,2] an alternative explanation to be considered implies that the sharp increase in k_2(obs) observed above $pH_{app} \sim 13$ in the oxidation of DPPO with PBA (see Fig 1, ref 2) might actually be due to the reaction of ionized phosphine oxide molecule $(Ph_2P{=}O)^-$ on $C_6H_5C(:O)O{-}O^-$. Examples of attack by negatively charged nucleophiles on molecules which are isoelectronic with peroxyanions can be found in the literature,[9] and the nucleophilic reactivity of diarylphosphine oxides in basic media is also documented.[10,11]

EXPERIMENTAL

Materials and solvents. Diphenylphosphine oxide, bis-*p*-tolylphosphine oxide samples have been described: *p*-nitroperoxybenzoic acid (m.p. 136–137° [dec]) was synthetised by reaction of pure *p*-nitro-benzoic acid with 98% H_2O_2 (a gift from FMC Corp.) in $MeSO_3H$ and purified according to a reported method.[12] Pure t-butyl hydroperoxide was obtained starting from a commercial sample (Schuchardt, $\simeq$ 80% *t*-BuOOH content) by several consecutive vacuum fractional distillations (b.p. 35–36°/20 mm). Commercial 32% H_2O_2 (C. Erba, RP-ACS), AnalaR grade KOH and EDTA disodium salt (Merck) were used to make standard solns. Dioxan and water solvents were purified according to standard procedures.[1]

Kinetics. Rate constants were measured at 25·00° ± 0·05° by following the change in peroxide concentratn with time according to the technique already reported.[1–3] In the range of pH_{app} from 7·5 to 13·0, the pH of reactn mixtures was adjusted to the required value by addition of 0·1 M KOH aliquots and continuously monitored through each experiment with a glass electrode: the pH was kept constant to ±0·05 unit by the further addition of alkali soln, which was performed automatically by an autoburette ABU-11 connected with a titrator TTT-11b and a pH-meter PHM-26c (all Radiometer models), used as a pH-stat. Rate constants which appear in Tables 1 and 2 are usually average values (±5%) from two or more independent runs. Values of H_- for several KOH concentrations in the mixed solvent employed were obtained by the spectrophotometric technique already described.[2] In dioxan–water 40:60, for KOH concentrations ranging from 0·0015 to 0·400 M, in agreement with the Eq. $H_- = pK_w + \log[OH^-]$,[13] a plot of H_- *vs* $\log[OH^-]$ was linear with slope 1·0 and intercept 15·08 ± 0·10. This, therefore, was taken as the pK'_w value in the mixed solvent used: it is in reasonable agreement with the pK_w values measured in a number of dioxan–water mixtures by Baughman and Gunwald.[14] The log K'_e values for t-BuOOH and HOOH in dioxan–water 40:60 were estimated through Eq. (11) by recording (on a Cary 15 or Gilford 2400 instrument) a number of UV spectra of the hydroperoxide at increasing KOH concentrations. The ε_{ROOH} and ε values were obtained directly from optical density readings (at 260 nm) and from the known peroxide concentrations: ε_{ROO^-} values, instead, were estimated from the intercept on plots of $1/\varepsilon$ *vs* $1/[OH^-]$.[13]

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