

Cetyltrimethylammonium hydroperoxide: an efficient reagent for promoting phosphate ester hydrolysis

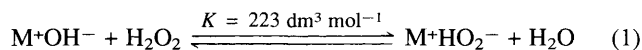
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Cetyltrimethylammonium hydroperoxide solutions are easily prepared by mixing cetyltrimethylammonium hydroxide and hydrogen peroxide and are very efficient in promoting paraoxon (diethyl *p*-nitrophenyl phosphate) hydrolysis.

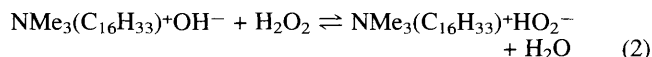
Over the last few years a great deal of work has been devoted to finding versatile and efficient decontaminants, capable of eliminating phosphate, phosphonate and phosphinate neurotoxic esters (pesticides or chemical warfare agents) from the environment.^{1,2} We report here that solutions of cetyltrimethylammonium hydroperoxide (CTAOOH) can be easily obtained by mixing commercially available cetyltrimethylammonium hydroxide (CTAOH) with hydrogen peroxide and that these solutions, combining the advantages of the reactivity of an α -effect nucleophile (HO_2^-) and of micelle catalysis, are very efficient in promoting the hydrolysis of organophosphorus esters. Kinetic data are reported for the hydrolysis of diethyl *p*-nitrophenyl phosphate (paraoxon), a fairly unreactive compound.

It has long been known that the reaction of alkali-metal hydroxides with hydrogen peroxide ($\text{p}K_{\text{a}} = 11.65^3$) afford almost quantitatively the alkali-metal hydroperoxide when H_2O_2 is used in large excess [eqn. (1)].³ This makes it possible to prepare fairly stable HO_2^- - H_2O_2 solutions. Hydroperoxide



ions are very reactive nucleophiles, being notably capable of promoting carboxylate and phosphate ester hydrolysis.⁴

Due to the high basicity of CTAOH, a similar reaction occurs when aqueous CTAOH and H_2O_2 solutions are mixed [eqn. (2)].



The solutions obtained are also fairly stable (*e.g.* a solution made from 0.4 mol dm^{-3} H_2O_2 and $5 \times 10^{-3} \text{ mol dm}^{-3}$ CTAOH was kept at room temperature for three days without significant degradation) and they are very efficient in promoting ester hydrolysis.

Fig. 1 shows the first-order rate constant k_{v} for paraoxon hydrolysis (Scheme 1) (measured by following the increase in absorbance at 400 nm due to 4-nitrophenolate formation) plotted against the stoichiometric hydrogen peroxide concentration (including HO_2^-) for a given surfactant concentration ($5 \times 10^{-3} \text{ mol dm}^{-3}$). The increase in rate constant is due to the replacement of HO^- ions by the more reactive HO_2^- ions. The levelling-off in k_{v} observed above $[\text{H}_2\text{O}_2]_{\text{st}} \text{ ca. } 0.05 \text{ mol dm}^{-3}$ reflects a complete shift of the equilibrium of eqn. (2) to the right-hand side. Fig. 1 also shows the pH values measured for the solutions. It is noteworthy that these are moderately basic at the highest hydrogen peroxide concentrations used, and less basic than CTAOH or NaOH solutions at the same concentration.

Fig. 2 [curve (a)] shows the dependence of k_{v} on CTAOOH concentration (initial CTAOH concentration) at $[\text{H}_2\text{O}_2] = 0.1 \text{ mol dm}^{-3}$. The rate profile observed is typical of what is

predicted for such reacting systems when reactive counter-ion surfactants are used to promote the reaction of moderately soluble substrates with nucleophiles⁴ (*e.g.* CTAF^{5,6} and CTAOH⁷). For concentrations higher than the CMC (*ca.* $1.5 \times$

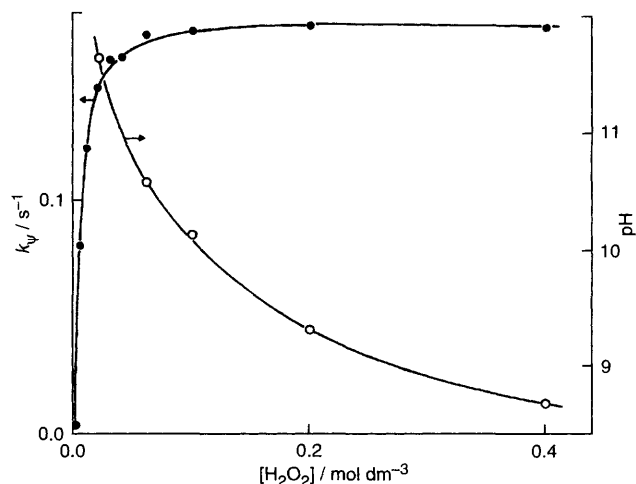
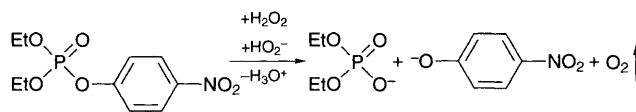


Fig. 1 Dependence of the first-order rate constant (25 °C) for paraoxon hydrolysis (●) on hydrogen peroxide concentration in the CTAOH- H_2O_2 system for $[\text{CTA}^+] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, and pH of the solutions (○)



Scheme 1 Paraoxon hydrolysis mediated by HO_2^-

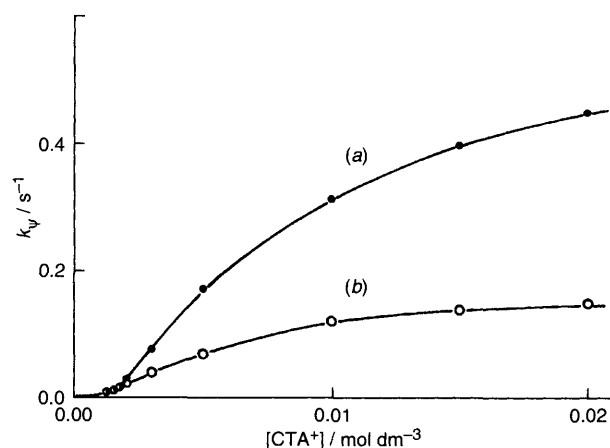


Fig. 2 Variations of the first-order rate constant (25 °C) for paraoxon hydrolysis with $[\text{CTA}^+]$ in CTAOH- H_2O_2 (●) and CTACl-NaOH- H_2O_2 systems (○) at constant stoichiometric concentration of H_2O_2 (0.15 mol dm^{-3}), the ratio between $[\text{CTA}^+]$ and $[\text{HO}_2^-]$ being kept constant and equal to unity

$10^{-3} \text{ mol dm}^{-3}$), the increase in rate is mainly due to a rise in solubilisation of the substrate in the micelles. These data show that the reaction is completed after a few seconds in the presence of CTAOOH. Data listed in Table 1 enable comparison of the rate constants observed at $[\text{CTAOOH}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ with those observed for CTAOH, NaOH and NaOOH at the same concentration, as well as the pH values corresponding to these solutions. The remarkable efficiency of the CTAOOH solutions is obvious. Moreover, the relatively low pH value at which the reaction occurs is a significant advantage for decontamination purposes.

The reaction of HO_2^- with diphenyl *p*-nitrophenyl phosphate (*ca.* 10^2 times more reactive than paraoxon) has been recently examined by Bunton and Foroudian⁸ in the presence of cetyltrimethylammonium chloride (CTACl) or mesylate (CTAOMs). Such reacting systems are alternatives for CTAOOH. However, since the reaction is believed to occur at the interface of the micelle pseudo-phase with the solution and since chloride or mesylate ions compete with hydroperoxide ions to be present at this interface, it is expected that the chloride or mesylate ions will inhibit the reaction of HO_2^- with phosphate esters, despite the fact that Cl^- and OMs^- are known to be readily replaced. In order to evaluate the differences in efficiency between the two kinds of reacting systems, we have measured the rate constants for paraoxon hydrolysis in CTACl– NaO_2H – H_2O_2 mixtures. Fig. 2 [curve (b)] shows the rate–concentration profile for concomitant variations of CTACl and HO_2^- concentrations ($[\text{CTACl}]/[\text{HO}_2^-] = 1$). The ratio between the rate constants for the CTAOOH– H_2O_2 and CTACl– HO_2^- – H_2O_2 systems reaches a value of *ca.* 3 for the highest surfactant concentrations used. This means that the affinity of Cl^- for association to the micelles is significantly larger than that of HO_2^- . In view of the data reported here it is likely that the affinity of HO_2^- ions *versus* Cl^- towards micelles is close to that reported⁹ for HO^- ions.‡

Table 1 Comparison of the first-order rate constants for paraoxon hydrolysis at the same concentration ($c = 5 \times 10^{-3} \text{ mol dm}^{-3}$) for different catalytic systems and pH values of the solutions

Catalytic system	$10^3 k_{\text{q}}/\text{s}^{-1}$	pH	k_{rel}^a
NaOH	0.0495	11.67	1
CTAOH	2.7	11.52	77
NaOOH– H_2O_2^b	3.1	10.23	1720
CTAOOH– H_2O_2^b	171	10.02	144000

^a Relative rate constants obtained as the ratios between k_{q} data and those estimated for NaOH solutions at same pH. ^b $[\text{H}_2\text{O}_2]_{\text{st}} = 0.1 \text{ mol dm}^{-3}$.

It can be argued that the fairly high commercial cost of CTAOH is a significant disadvantage for the use of the CTAOOH– H_2O_2 (CTAOH– H_2O_2) mixtures, compared with that of the CTACl– NaO_2H – H_2O_2 (CTACl–NaOH– H_2O_2) systems. However, we have found that the former surfactant can be easily and cheaply prepared from CTACl or CTABr. Cetyltrimethylammonium sulfate (or hydrogenosulfate) was obtained by the method suggested by Sepúlveda *et al.*¹⁰ for replacing the bromide ion in CTABr. CTAOH solutions were easily prepared by mixing cetyltrimethylammonium sulfate and barium hydroxide solutions and elimination of the barium sulfate precipitate.

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Footnotes

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‡ An exchange equilibrium constant $K_{\text{OH}}^{\text{Cl}}$ of 5, between bulk water and the micelle interface, has been reported.⁹

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