Kinetics of the Hydrolysis and Perhydrolysis of Tetraacetylethylenediamine, a Peroxide Bleach Activator

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Hydrogen peroxide and water react with tetraacetylethylenediamine (TAED) to form consecutively triacetylethylenediamine and diacetylethylenediamine with the release of two molecules of peracetic acid or acetic acid. The effect of pH, specific buffers and temperature on the rates of hydrolysis and perhydrolysis are compared. Peracetic acid reacts with TAED very slowly. The ratio of the second-order rate constants for the reaction of TAED with hydroperoxide and peracetate anions is exceptionally large after taking into account the difference in p*K*a values of their conjugate acids. The relative reactivity of various nucleophiles with TAED is discussed in terms of its performance as a bleach activator.

As bleaching agents, peracids are generally considered to be better than hydrogen peroxide. It was recognized almost forty years ago that acyl transfer from an 'activator' molecule to hydrogen peroxide to yield a peracid should improve the performance of the peroxide bleaching system.[1] Activated bleaching is now feasible utilizing added polyaminomethylenephosphonates to suppress the undesirable reaction of hydrogen peroxide and peracid, which is catalysed by trace metal ions.[2,3]

We have recently studied *p*-nitrophenyl acetate as a model bleach activator.[4,5] The peracid formed during the perhydrolysis of the ester reacts with the ester to form diacetyl peroxide which then undergoes hydrolysis or perhydrolysis yielding, respectively, one or two molecules of peracetic acid. The formation of acetic acid from the hydrolyses of ester and diacetyl peroxide represents an undesirable wastage of the activator. We now report on the commercially important imidic bleach activator tetraacetylethylenediamine (TAED). The present results show that the TAED–hydrogen peroxide system differs significantly from the ester system previously studied.

Experimental

Materials.—Ethylenediaminetetramethylenephosphonic acid (EDTMP)·H_2O (92:8) and tetra-, tri-, and di-acetylethylenediamine (TAED, TriAED and DAED), respective purities 99%, 98% and >99%, were provided by Warwick International Ltd. Peracetic acid (Proxitane 4002) was donated by Interox Chemicals Ltd. Hydrogen peroxide was removed from the Proxitane simply by raising the pH of a diluted solution to 10.5 and leaving for 5 min before adjusting the pH to the required value.[5] Kinetic runs were carried out within 1 h of the pH adjustment. Sodium carbonate, sodium hydrogen carbonate and hydrogen peroxide (30% w/v) were Analar reagents. Solutions were made up in distilled water.

Methods.—Stock solutions of hydrogen peroxide and peracetic acid were standardized by cerimetric and iodimetric titration. Absorbances were measured using a Hewlett Packard HP 8451A diode-array spectrophotometer fitted with a thermostated cell holder. Reactions were carried out in carbonate buffers, ionic strength 0.1 mol dm^{-3}, at 25 °C unless stated otherwise. Buffers contained 1×10^{-5} mol dm^{-3} EDTMP to suppress the reaction between hydrogen peroxide and peracetic acid.[2,3] Aliquots of reaction solution were taken to determine the sum of the peracid and hydrogen peroxide concentrations and the peracid concentration as described previously.[6] Aliquots were also taken and diluted 21-fold with distilled water to reduce the background absorbance of the buffer in the UV region in order to obtain sequential spectra. In some runs the reactions were followed in the cuvette at 232 nm and, in order to minimize photodegradation of hydrogen peroxide and the ensuing reactions involving carbonate buffer and possibly other species, relatively few, *ca.* 20–30, absorbance readings were taken over *ca.* four half-lives. The hydrolysis of peracetic acid was monitored by assaying aliquots of the solution for hydrogen peroxide using the Ti^{IV} method.[7]

Determination of Rate Constants.—The hydrolysis of TAED is biphasic and rate constants were calculated by non-linear regression of eqn. (1), where $A(\lambda_i)$ is absorbance at λ_i nm,

$$A(\lambda_i) = A_\infty(\lambda_i) + A_1(\lambda_i)\exp(-k_1 t) + A_2(\lambda_i)\exp(-k_2 t) \quad (1)$$

values of λ_i range from 194–230 nm at 4 nm intervals and $A_\infty(\lambda_i)$ is the final absorbance of the reaction solution that includes a contribution from the background absorbance, $A_B(\lambda_i)$ of the buffer. The spectrum of the intermediate, TriAED, was calculated using eqn. (2) with independently determined

$$\varepsilon_{TriAED}(\lambda_i) = \{A_\infty(\lambda_i) - A_B(\lambda_i) + A_2(\lambda_i)(k_1 - k_2)/k_1\}/[TAED]_0 - \varepsilon_{ac}(\lambda_i) \quad (2)$$

values of the background absorbance and the extinction coefficient of acetate, $\varepsilon_{ac}(\lambda_i)$. The perhydrolysis of TAED was followed under pseudo-first-order conditions with excess hydrogen peroxide by monitoring the formation of peracid. The rate constant for the perhydrolysis of TriAED was obtained by a numerical analysis[4,5] that is described later. In a subsequent series of runs the perhydrolysis of TriAED was monitored at 232 nm by following the slow phase of the reaction of TAED and excess hydrogen peroxide and the rate constant was calculated by non-linear regression of eqn. (3).

$$A = A_\infty + A_2\exp(-k_2 t) \quad (3)$$

The initial rates of reaction, R_0, of TAED and peracid were calculated from absorbances at 216 nm of sequential aliquots of the reaction solution diluted 21-fold with water according to

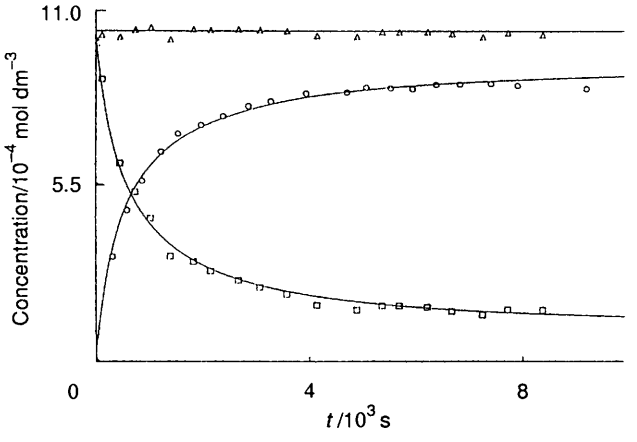

Fig. 1 Time course of the reaction of TAED, 5×10^{-4} mol dm^{-3}, and hydrogen peroxide, 1×10^{-3} mol dm^{-3} in carbonate buffer, pH 9.6; [EDTMP] 1×10^{-5} mol dm^{-3}. Peracetic acid, ○; peracetic acid plus hydrogen peroxide, △; hydrogen peroxide calculated from the previous concentrations, □. The curves are numerical solutions of the differential equations corresponding to eqns. (5)–(8) using the kinetic parameters given in Table 1.

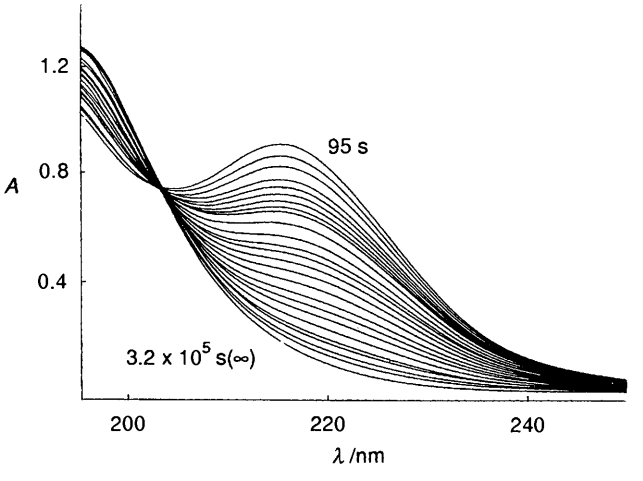

Fig. 2 Sequential spectra, after 21-fold dilution, of the hydrolysis of TAED, 1×10^{-3} mol dm^{-3}, in carbonate buffer, pH 10.47

eqn. (4) in which $\Delta\varepsilon$ is the difference in extinction coefficients of TAED and TriAED, 17 200 and 8710 dm^3 mol^{-1} cm^{-1}, respectively. Kinetic parameters are given with their 90% confidence limits.

$$R_0 = \frac{2l}{\Delta\varepsilon}\left(\frac{dA}{dt}\right)_0 \equiv -\left(\frac{d[TAED]}{dt}\right)_0 \quad (4)$$

Results

Stoichiometry.—Fig. 1 shows that, when hydrogen peroxide and TAED are mixed in a 2:1 mole ratio, in the presence of EDTMP, no peroxide decomposition occurs and the fall in hydrogen peroxide mirrors the formation of peracetic acid. Somewhat less than 2 mol of peracid are formed per mole of TAED which indicates that hydrolysis and perhydrolysis are occurring, eqns. (5)–(8). Separate experiments with isolated DAED show that it is inert.

$$\underset{\text{TAED}}{(CH_3CO)_2N(CH_2)_2N(OCCH_3)_2} + H_2O \xrightarrow{k_{H_2O}^{TAED}} \underset{\text{TriAED}}{CH_3CONH(CH_2)_2N(OCCH_3)_2} + CH_3CO_2H \quad (5)$$

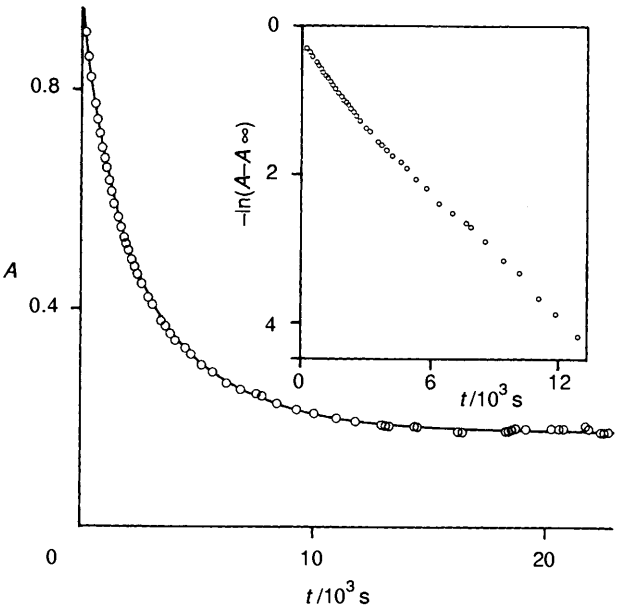

Fig. 3 Plots of (after 21-fold dilution) A (216 nm), and ln $\{A(216\text{ nm}) - A_\infty(216\text{ nm})\}$ *versus* t during the hydrolysis of TAED, 1×10^{-3} mol dm^{-3}, in carbonate buffer, pH 10.47 The solid line is calculated from eqn. (1).

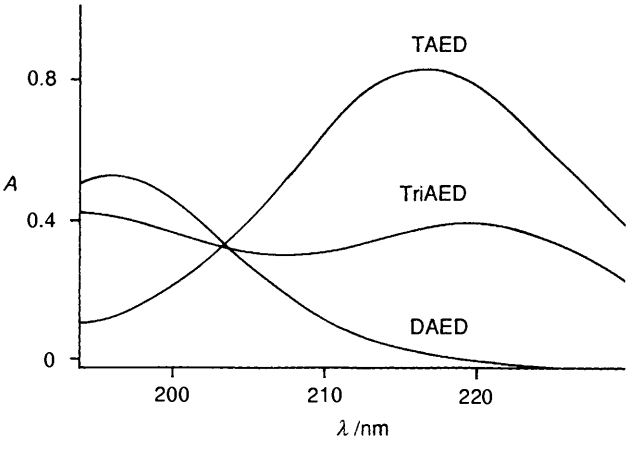

Fig. 4 Spectrum of TriAED, 4.76×10^{-5} mol dm^{-3}, calculated from eqn. (2). Spectra of equimolar solutions of TAED and DAED are included for comparison.

$$\underset{\text{TriAED}}{} + H_2O \xrightarrow{k_{H_2O}^{TriAED}} \underset{\text{DAED}}{CH_3CONH(CH_2)_2HNOCCH_3} + CH_3CO_2H \quad (6)$$

$$\text{TAED} + H_2O_2 \xrightarrow{k_{H_2O_2}^{TAED}} \text{TriAED} + CH_3CO_3H \quad (7)$$

$$\text{TriAED} + H_2O_2 \xrightarrow{k_{H_2O_2}^{TAED}} \text{DAED} + CH_3CO_3H \quad (8)$$

Hydrolysis.—Fig. 2 shows the drop in absorbance of TAED and a corresponding rise in absorbance at lower wavelengths due to the formation of DAED. The isosbestic point at 203.5 nm is unexpected since the log$A$ *versus* t plot shown in the insert to Fig. 3 indicates that the reaction is biphasic. However, treatment of the data according to eqns. (1) and (2) yields the spectrum of the intermediate shown in Fig. 4 (which is identical to a sample of isolated TriAED that was provided by Warwick International Ltd. after this study was completed) and it is evident that at the isosbestic point the extinction coefficients

Table 1 Rate constants for the hydrolysis and perhydrolysis of TAED and TriAED in carbonate buffers, ionic strength 0.1 mol dm^{-3}; *T*, 25 °C; [EDTMP] 1 × 10^{-5} mol dm^{-3}

pH	$k_{H_2O}^{TAED}/10^{-4}$ s^{-1}	$k_{H_2O}^{TriAED}/10^{-4}$ s^{-1}	$k_{H_2O_2}^{TAED}$/dm^3 mol^{-1} s^{-1}	$k_{H_2O_2}^{TriAED}$/dm^3 mol^{-1} s^{-1}
9.60	1.40	0.50	3.35[a]	1.16
10.47	7.09	2.57	—	—

[a] Five runs; 90% confidence limits, ±0.11.

Table 2 Second-order rate constants for the reaction between TriAED and hydrogen peroxide in carbonate buffers, I = 0.1 mol dm^{-3}; [EDTMP] 1 × 10^{-5} mol dm^{-3}

T/°C	pH	$k_{H_2O_2}^{TriAED}$/dm^3 mol^{-1} s^{-1}
25	9.60	1.16 ± 0.16[a]
25	9.99	2.8 ± 0.3[a]
25	10.47	8.4 ± 0.6[a]
15.15	10.09	1.7 ± 0.1[a]
35	9.85	5.7 ± 1.1[a]
39.4	9.77	7.9 ± 0.6[a]
50.7	9.62	16 ± 3[a]

[a] ±90% confidence limits; number of runs 4 or 5.

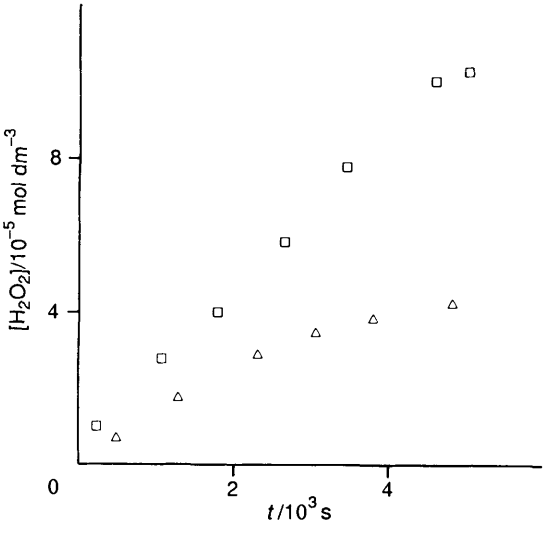

Fig. 5 Release of hydrogen peroxide from peracetic acid, 5.54 × 10^{-3} mol dm^{-3} in pH 9.6 carbonate buffer in the presence □, and absence △ of EDTMP, 1 × 10^{-5} mol dm^{-3} at room temperature

of TAED, DAED and TriAED are all very similar. Rate constants calculated according to eqn. (1) with $k_1 \equiv k_{H_2O}^{TAED}$ and $k_2 \equiv k_{H_2O}^{TriAED}$ are included in Table 1 and an illustration of the fit to eqn. (1) at a single wavelength is shown in Fig. 3.

Perhydrolysis.—Using concentrations of hydrogen peroxide and TAED of 4.5 × 10^{-5} and (5.0–9.0) × 10^{-4} mol dm^{-3} plots of $\ln\{[CH_3CO_3H]_\infty - [CH_3CO_3H]\}$ *versus* *t* are linear for at least four half-lives and the pseudo-first-order rate constants are directly proportional to the concentrations of TAED (results not shown) and yield the value of $k_{H_2O_2}^{TAED}$ included in Table 1. Since the rate of reaction of TAED and peracetic acid is negligible the value of $k_{H_2O_2}^{TriAED}$ included in Table 1 is obtained from the data of Fig. 1 by numerical solution of the differential equations corresponding to eqns. (5)–(8) using the initial concentrations, the values of $k_{H_2O}^{TAED}$, $k_{H_2O_2}^{TriAED}$ and $k_{H_2O_2}^{TAED}$ and varying $k_{H_2O_2}^{TriAED}$ until the best-fit curves shown on the figure are obtained.

Using concentrations of TAED and hydrogen peroxide of 1 × 10^{-4} and (1.0–15.0) × 10^{-3} mol dm^{-3}, values of k_2 according to eqn. (3) are directly proportional to the concentration of hydrogen peroxide, gradient ≡ $k_{H_2O_2}^{TriAED}$, and the 90% confidence limits of the almost zero intercept include the value of $k_{H_2O}^{TriAED}$ (results not shown). The pH and temperature dependence of $k_{H_2O_2}^{TriAED}$ is shown in Table 2. The value of the rate constant at 25 °C with respect to concentration of the hydroperoxide anion using[8] pK_a, 11.6 in eqn. (9) is $k_{HOO^-}^{TriAED}$

$$k_{nuc}^{activator} = k_{nucH}^{activator}(K_a + [H^+])/K_a \quad (9)$$

118 ± 6 dm mol^{-3} s^{-1}, independent of pH and buffer composition. Taking into account the temperature dependence of K_a,[9] the activation parameters for the reaction of the hydroperoxide anion and TriAED are $\Delta H^\ddagger$, 36 ± 8 kJ mol^{-1} and $\Delta S^\ddagger$, −82 ± 29 J mol^{-1} K^{-1}.

Peracetolysis.—Preliminary experiments showed that the reaction of TAED and peracetic acid is slow and that a significant contribution to the overall rate of loss of TAED is due to its reaction with hydrogen peroxide formed from the hydrolysis of the peracid. Fig. 5 shows the hydrolysis of peracetic acid. In the absence of EDTMP the concentration of hydrogen peroxide approaches a limiting value due to its trace metal-ion-catalysed reaction with the peracid. In the presence of EDTMP the amount of hydrogen peroxide increases linearly with *t* yielding a rate constant $k_{H_2O}^{PA}$ 3.7 × 10^{-6} s^{-1}. The initial rate of reaction of TAED, R_0, in the presence of peracetic acid is given by eqn. (10), which uses a steady state approximation in the concentration of hydrogen peroxide since $k_{H_2O}^{TAED}[TAED]_0 \gg k_{H_2O}^{PA}[PA]_0$.

$$R_0 = k_{H_2O}^{TAED}[TAED]_0 + k_{PA}^{TAED}[TAED]_0[PA]_0 + k_{H_2O}^{PA}[PA]_0 \quad (10)$$

Using concentrations of TAED and peracetic acid of 1 × 10^{-3} and (1.8–5.3) × 10^{-3} mol dm^{-3} a plot (not shown) of R_0 *versus* initial peracid concentration has intercept (1.8 ± 0.6) × 10^{-7} mol dm^{-3} s^{-1} and gradient (4.1 ± 1.6) × 10^{-5} s^{-1} yielding k_{PA}^{TAED} (3.8 ± 1.6) × 10^{-2} dm^3 mol^{-1} s^{-1}.

Discussion

TAED undergoes hydrolysis and perhydrolysis to form TriAED and DAED consecutively. Table 1 shows that, after correction for the statistical factor of two, TAED is slightly more reactive than TriAED toward nucleophiles. This reflects the additional electron-withdrawing acetyl group on TAED. The low reactivity of DAED is typical of amides and due to resonance stabilization of the amide bond. In TAED and TriAED delocalization of the nitrogen lone pair occurs over both carbonyl functions hence reducing the strength of the N–C bond relative to that of amides. The enhanced rate of hydrolysis of imides is well documented.[10–15]

A detailed study of the hydrolysis of *N*-methyldiacetamide, which is structurally very similar to TAED and TriAED, has been reported by Laurent and Pellissier.[11] These authors propose a mechanism in which attack of hydroxide on the carbonyl carbon is followed by general-acid-catalysed breakdown of the tetrahedral intermediate wherein at high HCO_3^- concentrations the rate becomes independent of buffer

concentration reflecting rate limiting attack of hydroxide. The variation with pH of the rate constants for the hydrolysis of TAED and TriAED (Table 1 and results not shown) are consistent with the mechanism proposed by Laurent and Pellissier.

In contrast to the hydrolysis reactions, we find no evidence for general acid catalysis during the reaction of TriAED and the hydroperoxide anion since $k_{HOO^-}^{TriAED}$ is independent of buffer composition. Moreover, because HOO^- is a much better nucleophile than HO^-, rate limiting attack by HOO^-, as is the case with HO^- at high HCO_3^- concentration, is improbable and we conclude that the perhydrolysis of TriAED is not general-acid catalysed. The entropy of activation for the perhydrolysis, -82 ± 29 J mol^{-1} K^{-1}, is significantly less negative than the value -136 J mol^{-1} K^{-1} which can be calculated from the data of Laurent and Pellissier for the reaction of HO^- and *N*-methyldiacetamide in the absence of added general-acid catalysts. Thus the mechanisms of hydrolysis and perhydrolysis differ significantly and structure–reactivity relationships for hydrolysis of imidic compounds[10–15] may not reflect those for perhydrolysis. This is pertinent to predicting the efficiency of various possible bleach activators where the ratio of the rates of perhydrolysis to hydrolysis should be a maximum.

The absence of buffer effects in the perhydrolysis of TriAED is in contrast to our previous study of the model bleach activator *p*-nitrophenyl acetate.[4,5] Buffer effects were observed for the perhydrolysis of the ester but not for its reaction with peracetic acid. This was interpreted as an interaction of a basic component of the buffer with the hydrogen atom of HO_2^- in the activated complex. Clearly the perhydrolysis of TriAED does not proceed *via* a similar mechanism since it is not general-base catalysed.

The most striking feature of the present results is the ratio of reactivity of TAED with HOO^- and peracetate, $k_{HOO^-}^{TAED}/k_{PA^-}^{TAED}$ 9.1×10^6 compared with 34 for the corresponding ratio with *p*-nitrophenyl acetate,[4,5] and bearing in mind that the ratio of the acid dissociation of hydrogen peroxide (pK_a 11.6)[8] and peracetic acid (pK_a 8.2)[8] is 2.5×10^4. Reactivity ratios are a form of linear free energy relationship, which have traditionally been used as a measure of the amount of bond formation and breaking in the activated complex.[16,17] The difference in reactivity ratios noted above reflects the poor leaving group character of the amido function of TAED compared to *p*-nitrophenyl acetate but, nevertheless, the reactivity ratio for TAED is rather high considering the difference in pK_a values of the conjugate acids of the nucleophiles, and other factors may need to be considered. It is not apparent whether the greater reactivity towards peracid of ester-type bleach activators compared with amidic ones constitutes an advantage with respect to bleach activation: the diacyl peroxide that is formed providing additional bleaching pathways. It is clear, however, that the subsequent rapid hydrolysis of the diacyl peroxide[4,5] represents an additional pathway contributing to the undesirable hydrolysis of the activator.

Finally, it is of note that a similar correlation exists between the rate of alkaline hydrolysis of peracetic acid (this paper) and those of a range of substituted perbenzoic acids[18] as exists between the rate of reaction of peracetic acid[4,5] and a range of substituted perbenzoic acids[19] with *p*-nitrophenyl acetate.

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