Structure–reactivity correlation for reactions of peroxide anion nucleophiles with substituted acyloxybenzenesulfonate bleach activators

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Second-order rate constants are reported for the reaction between a series of esteric bleach activators with different acyl substituents, namely, acetyloxybenzenesulfonate, *n*-butanoyloxybenzenesulfonate, *n*-nonanoyloxybenzenesulfonate and isononanoyloxybenzenesulfonate, and a set of peroxide nucleophiles whose basicity ranges from below that of the oxybenzenesulfonate leaving group to above it. The results conform to a Brønsted-type relationship with β_{nuc}, 0.42 ± 0.01 for acetyloxybenzenesulfonate, very similar to the value of 0.40 ± 0.01 for *para*-nitrophenyl acetate and a range of peroxide nucleophiles. A significantly larger value of β_{nuc}, 0.56 ± 0.05 is obtained with *n*-nonanoyloxybenzenesulfonate. This increase in β_{nuc} is interpreted in terms of steric and polar interactions between the acyl substituent and the attacking nucleophile. The reactivity of *n*-butanoyloxybenzenesulfonate is similar to that of *n*-nonanoyloxybenzenesulfonate whilst that of isononanoyloxybenzenesulfonate is less. These results are discussed in terms of the practical consequences for bleach activation and with regard to the mechanism of acyl transfer from esters to peroxides.

The function of peroxide bleach activators is to transfer an acyl group to the hydroperoxide anion, HOO^-. In the process the activator undergoes perhydrolysis to form a peracid (acyl hydroperoxide) that is a better oxidant than hydrogen peroxide itself.[1] Peroxide bleach activators are used in detergents, biocides, industrial bleaching, effluent treatment, and environmental remediation. The two most commercially important peroxide bleach activators are tetraacetylethylenediamine (TAED) and sodium *n*-nonanoyloxybenzenesulfonate. The former is an imidic compound that yields two molecules of peracetic acid on perhydrolysis; the latter ester yields pernonanoic acid. The biphasic kinetics of the perhydrolysis of TAED has been described.[2] The mechanism of perhydrolysis of imidic type activators has been studied by means of linear free energy relationships using triacetylethylenediamine as a model of TAED because of its simpler monophasic kinetics.[3] Typical behaviour[4] was observed for triacetylethylenediamine with a range of nucleophile families whose members were all less basic than the amide anion leaving group. The basicity of the nucleophile and the leaving group are defined as the pK_a of their conjugate acids, pK_{nuc} and pK_{lg}, respectively. Peroxide anions are α-nucleophiles,[5–8] and were the most reactive.[3] The hydroperoxide anion was exceptionally reactive among the peroxide anion nucleophiles and this was explained in terms of a cyclic activated complex in which the hydrogen of the hydroperoxide anion protonates the amide anion leaving group.[3]

Previous systematic studies of acyl transfer from esters to peroxide anion nucleophiles, eqn. (1), have involved *para*-

$$R{-}CO{-}OC_6H_4Y + {}^-OOX = R{-}CO{-}OOX + {}^-OC_6H_4Y \quad (1)$$

nitrophenyl acetate[6,7,9] (PNPA, R = Me, Y = 4-NO_2) pK_{lg} 7.14.[10] The present study also uses the sodium salts of acetyloxybenzenesulfonate, (SAOBS, R = Me), *n*-butanoyloxybenzenesulfonate [S*n*BOBS, R = $(CH_2)_2Me$], *n*-nonanoyloxybenzenesulfonate [S*n*NOBS, R = $(CH_2)_7Me$] and isononanoyloxybenzenesulfonate [SiNOBS, R = $CH_2CHMeCH_2C(Me)_3$] all with Y = 4-SO_3^-, pK_{lg}, 9.06.[10] The peroxide nucleophiles used are peracetate, peroxomonosulfate, hydroperoxide anion and peroxomonophosphate, X = COMe, SO_3^-, H and PO_3^{2-}, respectively, whose basicity range from below that of the oxybenzenesulfonate leaving group to above it. The sensitivity of the rate constant to the basicity of the leaving group and the nature of the acyl substituent, R, of the activator, and to the basicity of the peroxide is discussed in terms of the practical consequences for bleach activation and with regard to the mechanism of acyl transfer from esters to peroxides.

Experimental

Materials

Sodium *n*-nonanoyloxybenzenesulfonate, 97%, sodium isononanoyloxybenzenesulfonate, 67%, sodium *n*-butanoyloxybenzenesulfonate, 97%, and sodium acetyloxybenzenesulfonate, 67%, were provided by Warwick International Group Ltd. The major impurity associated with the esters is sulfonated phenol. *para*-Nitrophenyl acetate, 97%, aqueous hydrogen peroxide, 27.5 wt%, aqueous peracetic acid, 36–40 wt%, and potassium peroxomonosulfate triple salt, $2KHSO_5{\cdot}K_2SO_4{\cdot}KHSO_4$ were purchased from Aldrich. Potassium peroxodiphosphate, $K_4P_2O_{10}$, 86%, was provided by Interox Ltd. Carbonate buffer components were AnalaR reagents. Solutions were made up in distilled water. Peracid solutions were made up daily. Hydrogen peroxide was removed from the aqueous peracetic acid before use by raising the pH of a diluted solution to 10.5 for 5 minutes before adjusting, if necessary, to the working pH.[9] The hydrolysis of the peracetic acid is negligible under the conditions of the experiments.[2] Peroxomonophosphate was prepared by the hydrolysis of peroxodiphosphate in dilute sodium hydroxide. Concentrations of stock peracid solutions were determined by iodometric titration and working solutions obtained by dilution.

Kinetics

Kinetic runs were carried out in carbonate buffer, ionic strength 0.1 mol dm^{-3} at 25 °C. Reactions were followed using a Hewlett-Packard HP 8415A spectrophotometer with a thermostatic cell holder, monitoring the rise in absorbance, *A*, due to the release of the *para*-nitrophenolate anion at 400 nm or the oxybenzenesulfonate anion at 254 nm. A limited number of measurements were made to minimise photodegradation reactions.[3]

Table 1 Rate constants for the reactions of peroxide anion nucleophiles with *para*-nitrophenyl acetate and alkoxybenzenesulfonates in carbonate buffers, ionic strength 0.1 mol dm^{-3}, 25 °C

		k_{nuc}/dm^3 mol^{-1} s^{-1}				
Peroxide	pK_a(nucH)	PNPA	SAOBS	S*n*BOBS	S*n*NOBS	SiNOBS
$^{2-}O_3POO^-$	12.8[a]				1500	
HOO^-	11.6[b]	3800[e]	860	440	430	140
$^-O_3SOO^-$	9.3[c]		63		9.7	
CH_3COOO^-	8.2[d]	113	24	6.4	5.3	

[a] From E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 2263. [b] From M. G. Evans and N. Uri, *J. Chem. Soc., Faraday Trans.*, 1949, **45**, 224. [c] From D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, 1955, **78**, 1125. [d] From A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, 1953, **49**, 410. [e] From ref. 9.

Pseudo-first-order conditions with the peroxide in excess were used and the observed first-order rate constant obtained from linear regression of ln $(A - A_\infty)$ against time. At least five different concentrations of each peroxide were used and the second order rate constant under the experimental conditions (k_2) calculated as the slope ± standard deviation of a linear regression of observed rate constant *versus* concentration.[3] The rate constants with respect to the concentration of the peroxide anion nucleophile, k_{nuc}, were calculated using eqn. (2) and the

$$k_{nuc} = k_2 (K_a + [H^+])/K_a \qquad (2)$$

pK_a values that are shown in Table 1. The actual working pH's of the kinetic runs were 9.2 for PNPA, 10.0 for SAOBS, 9.9 and 10.3 for S*n*BOBS with hydrogen peroxide and peracetic acid respectively, 9.5 for S*n*NOBS with hydrogen peroxide and peracetic acid, 10.5 for S*n*NOBS with peroxomonophosphate and peroxomonosulfate and 9.5 for SiNOBS.

Results

Plots of the observed pseudo-first-order rate constants were directly proportional to the peroxide concentration with negligible intercepts, showing that the contribution of hydrolysis to the overall rate was negligible and standard deviations of k_2 were generally less than 5% of the best fit value (results not shown). Values of k_{nuc} are shown in Table 1. The value of k_{nuc}, for the reaction of *para*-nitrophenyl acetate and the peracetate anion was obtained in carbonate buffer under conditions very similar to those used previously for *meta*- and *para*-substituted perbenzoates[7] and the hydroperoxide anion.[9] Fig. 1 includes a Brønsted-type plot for these data using the statistically corrected pK_a of hydrogen peroxide. Regression analysis of these values yields a Brønsted slope ± standard deviation of β_{nuc}, 0.40 ± 0.01. The corresponding Brønsted slope for acetyloxybenzenesulfonate (SAOBS) is, β_{nuc}, 0.42 ± 0.01. Hence the dependence of β_{nuc} on pK_{lg}, p_{xy} in the nomenclature of Jencks,[11] is equal or close to zero. Also, Fig. 1 shows no evidence for a decrease in β_{nuc} with increasing pK_{nuc} for the acetyloxybenzenesulfonate reaction, hence p_x[11] is equal or close to zero. The rate constants with acetyloxybenzenesulfonate are lower than those with *para*-nitrophenyl acetate and Brønsted slopes for leaving groups, β_{lg}, comparing rate constants for *para*-nitrophenyl acetate (pK_{lg} 7.14)[10] and acetyloxybenzenesulfonate (pK_{lg} 9.06)[10] are −0.35 for peracetate and −0.33 for the hydroperoxide. Thus the dependence of β_{lg} on the pK_{nuc}, another measure of p_{xy},[11] is equal or close to zero. The reaction of *n*-nonanoyloxybenzenesulfonate with peroxides is slower than that of acetyloxybenzenesulfonate and a value of β_{nuc}, 0.56 ± 0.05 is obtained that is significantly larger than the value of 0.42 ± 0.01 for acetyloxybenzenesulfonate, Fig. 1. Moreover the standard deviation is larger and there is evident scatter in the Brønsted-type plot. The rate constants for the reaction of *n*-butanoyloxybenzenesulfonate with the hydroperoxide anion and peracetate, respectively, are similar to those of *n*-nonanoyloxybenzenesulfonate as shown in Table 1, but they are not included in Fig. 1 for the sake of clarity. The rate constant for the reaction of isononanoyloxybenzenesulfonate with the hydroperoxide anion, Table 1, is significantly lower than that of *n*-nonanoyloxybenzenesulfonate.

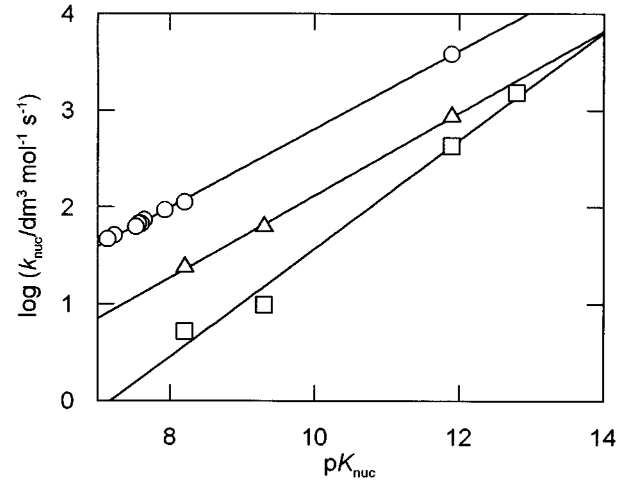

Fig. 1 Brønsted-type correlations for the reactions of peroxide anion nucleophiles with PNPA (○) including data for substituted perbenzoates, ref. 7; SAOBS (△) and S*n*NOBS (□)

Discussion

Peroxide bleach activation

A previous study of *para*-nitrophenyl acetate as a model esteric bleach activator demonstrated that after the initial attack of a hydroperoxide anion on the ester then the peracetate anion product also attacks the ester to form diacetyl peroxide which, in its turn, is attacked by a second hydroperoxide anion to yield two peracid moieties.[9] This behaviour with regard to diacyl peroxide formation is not unexpected considering the low β_{nuc} for *para*-nitrophenyl acetate shown in Fig. 1. The present results show that diacyl peroxide formation is also feasible for the oxybenzenesulfonate activators since they also have low β_{nuc} values. These results could not have been predicted in advance because, for example, Brønsted plots for acyl transfer to nucleophiles such as thiolates show a break close to pK_{lg} and have a much greater β_{nuc} value for nucleophiles of lower pK_{nuc}.[12] This point will be discussed further in the next section. Suffice it to say in the present context that the alkyloxybenzenesulfonate activators used in this study show no evidence of breaks in the Brønsted plots. In contrast to the esteric bleach activators, diacyl peroxide formation is not feasible for imidic activators such as TAED, for which the hydroperoxide anion is a very much better nucleophile than are the peracid anions.[2,3]

Mechanism of acetyl transfer to peroxides

The rate constants described here for the reaction of the peroxide anion nucleophiles with *para*-nitrophenyl acetate are higher than those of thiolates,[12] amines,[13] phenolates,[13–15] alcoholates[13,16] and other oxygen nucleophiles.[8,13] This is consistent with the α-nucleophilicity of the peroxide anions. The values of β_{nuc} are 0.40 ± 0.01 and 0.42 ± 0.01, respectively, for the reactions of *para*-nitrophenyl acetate and acetyloxybenzenesulfonate with a range of peroxide nucleophiles and so are essentially independent of the nature of the leaving group. Moreover, these values of the Brønsted slopes do not change significantly as the basicity of the nucleophile increases from below that of the leaving group to above it. This behaviour compares with that of other nucleophiles in reaction with substituted phenyl acetates as follows. Acetyl transfer to thiol anions, in contrast to the peroxides, shows a well-defined break close to pK_{lg} with β_{nuc} around 0.8 below the break and 0.3 above the break.[12] This is indicative of a change in rate limiting step from attack of the nucleophile to breakdown of the tetrahedral intermediate. Acetyl transfer to amines shows a break at some four to five pK_a units above pK_{lg} and so is only observed for leaving groups with pK_{lg} values lower than *para*-nitrophenyl acetate. Here β_{nuc} changes from about 0.9 before the break to approximately 0.2 afterwards.[13] As with the thiolates, this has been interpreted as a change in the rate limiting step.[17] With phenolate nucleophiles, as with the peroxide nucleophiles described here, there is no break in the Brønsted plot in going through pK_{lg} but, in contrast with the peroxide nucleophiles, β_{nuc} changes systematically with pK_{lg} from about 0.6 with good leaving groups to about 1.0 for poorer leaving groups, although the precise variation seems to depend on the choice of nucleophiles.[15,18,19] Similarly, β_{lg} varies from about -0.8 with poor nucleophiles to -0.3 with better nucleophiles.[14,15,18,19] This is consistent with a concerted mechanism in which there is significant interaction between leaving and attacking groups. The following conclusions with regard to the reaction of peroxide anion nucleophiles with substituted phenyl acetates can be drawn from the above comparisons. Firstly, unlike the situation for thiolates, there is no evidence in terms of a change in rate limiting step for a reaction involving a tetrahedral intermediate. Nevertheless, as was the case for amine nucleophiles where proton basicity of the leaving group and nucleophile do not coincide with their basicity toward the carbonyl carbon, this cannot be ruled out. Secondly, there is no evidence, within experimental uncertainty, for a concerted mechanism of the sort observed for phenolate nucleophiles where there is significant interaction between leaving and attacking groups. Thirdly, the low values of β_{nuc} and β_{lg} are consistent with a reaction coordinate where the initial state is similar to the transition state. This is consistent with the fact that the peroxide nucleophiles are high energy reactants and acyl transfer to them results in high energy products.

Alkyl substituent effect

The effect of the alkyl substituents at the carbonyl carbon on the rate constant can be seen from Table 1. Increased chain length from acetyl to *n*-butanoyl causes a significant decrease in the rate constant whereas further increase in chain length to *n*-nonanoyl causes little further decrease. On the other hand, increased branching in going from *n*-nonanoyl to isononanoyl causes a decrease in the rate constant. These effects are consistent with polar and steric effects on an acyl transfer reaction that occurs *via* an associative mechanism. The increase in β_{nuc} in going from acetyloxybenzenesulfonate to the larger acyl groups (β_{nuc} is 0.56 ± 0.05 for *n*-nonanoyloxybenzenesulfonate) is evidence of an interaction term, $p_{xy'}$,[11] between the nucleophile and the alkyl substituent. Interaction terms are important for the characterisation of transition states of substitution reactions in general.[20] In the present case, the weaker the nucleophile (*i.e.* the lower pK_{nuc}) the later the transition state according to the Hammond postulate and the greater the sensitivity of the rate constant to alkyl substituent effects at the carbonyl carbon. Fig. 1 reflects these trends.

There is a general significance to the presence of an interaction term, $p_{xy'}$, between nucleophile and alkyl substituent. This is manifest in two ways. Firstly, for a series of nucleophiles of similar structure, attempts to measure β_{nuc} with a single acyl compound may lead to a result that contains systematic deviations due to interaction with the alkyl substituent. Hupe, and more recently, Jencks, have reported small differences in β_{nuc} for reactions between formate and acetate esters of nitrophenols and phenolate anion nucleophiles.[15,21] The corresponding difference between acetate and pivalate ($R = Bu^t$) is even more pronounced. The lower β_{nuc} for the bulkier alkyl group has been ascribed to solvation effects.[21] It is notable with regard to this that the β_{nuc} value for the reaction of thiol anions with *para*-nitrothiophenyl acetates and pivalates, respectively, is larger with the larger alkyl group. This is ascribed to the lower solvation of thiol anions.[21] The larger β_{nuc} values observed with larger alkyl groups in the present study may also reflect the lower solvation often ascribed to α-nucleophiles such as the peroxides.[8] The second way in which interation terms are manifest is for less structurally similar nucleophiles where use of a single acyl compound may lead to scatter in Brønsted plots that is not due to experimental error. This is observed as microscopic medium effects and is usually attributed to steric factors.[19]

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