991. *The Reaction of Substituted Peroxybenzoic Acids with Sodium o-Sulphobenzaldehyde and Sodium Sulphanilate in Aqueous Alkali.*

By P. Robson.

The reaction of substituted peroxybenzoic acids with sodium *o*-sulpho-benzaldehyde and sodium sulphanilate has been studied over a range of pH in aqueous solution. The kinetics of the reaction with sodium *o*-sulphobenz-aldehyde are of first order with respect to aldehyde and to peroxycarboxylate anion. The effect of substituents in the peroxyacid nucleus on reaction rate has been studied and a mechanism suggested which involves the formation of an intermediate state by an equilibrium process. The reaction of substituted peroxybenzoic acids with sodium sulphanilate is of first order with respect to amine and un-ionised peroxyacid. The substituent effects show the peroxyacid to be reacting electrophilically.

ALTHOUGH the action of peroxyacids on many organic compounds in non-aqueous media have been reviewed [1,2] and the mechanisms of most of them are now understood,[3–7] the reactions in water have received little attention. The kinetics and mechanism of the un-catalysed autodecomposition of peroxyacids have been described recently [8,9] and it is now possible to study their reaction with organic substrates under aqueous conditions since the extent of the accompanying autodecomposition can be estimated.

In this Paper, the reaction of a series of substituted peroxybenzoic acids with two alkali-soluble organic compounds, sodium *o*-sulphobenzaldehyde and sodium sulphanilate, has been examined. The study was carried out in sodium hydroxide solution in the absence of buffers because it has been shown that inorganic anions (*e.g.*, borax) may alter both the kinetics and mechanism of peroxyacid reactions.[8,10] During the reaction, as peroxyacid is consumed, the stronger parent carboxylic acid is produced. Slow addition of alkali is, therefore, necessary to fix the pH, which is monitored with a glass electrode. This technique has been described previously,[8] and the error introduced [11] is small when reactions are followed for short times. Small quantities of disodium ethylenediaminetetra-acetic acid (EDTA) were added to the reaction solutions to reduce, if not completely prevent, the catalytic decomposition of the peroxyacid caused by heavy-metal ions present as impurities in the alkali.[8]

EXPERIMENTAL

In the description of experimental work, all sections marked (*a*) refer to the reactions of peroxyacids with sodium *o*-sulphobenzaldehyde and those marked (*b*) to the reactions of peroxyacids with sodium sulphanilate.

Reagents.—*p*-Methoxy-, *p*-methyl-, and unsubstituted peroxybenzoic acid were prepared by the action of sodium methoxide on the appropriate diaroyl peroxide in chloroform–methanol mixtures. Purification of the peroxyacids was effected by vacuum sublimation.

p-Nitro- and *m*-chloro-peroxybenzoic acid were prepared from the parent carboxylic acid by the method of Silbert, Siegel, and Swern.[12] To obtain *p*-chloroperoxybenzoic acid, methyl *p*-chlorobenzoate was used. Peroxyacids prepared by this technique were generally >90% pure and were not purified further, the sole contaminant being the parent carboxylic acid.

[1] Swern, *Chem. Rev.*, 1947, **45**, 1.
[2] Davies, " Organic Peroxides," Butterworths, London, 1961.
[3] Bartlett, *Record Chemical Progress*, 1950, **11**, 47.
[4] Criegee, *Annalen*, 1948, **560**, 127.
[5] Hawthorne, Emmons, and McCallum, *J. Amer. Chem. Soc.*, 1958, **80**, 6393.
[6] Lynch and Pausacker, *J.*, 1954, 1131.
[7] Overberger and Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4250.
[8] Goodman, Robson, and Wilson, *Trans. Faraday Soc.*, 1962, **58**, 1846.
[9] Koubek, Haggett, Battaglia, Ibne-Rasa, Pyun, and Edwards, *J. Amer. Chem. Soc.*, 1963, **85**, 2263.
[10] Goodman and Robson, *J.*, 1963, 2871.
[11] Breuer and Jenkins, *Trans. Faraday Soc.*, 1963, **59**, 1310.
[12] Silbert, Siegel, and Swern, *J. Org. Chem.*, 1962, **27**, 1337.

The pK values of the peroxyacids were determined by potentiometric titration as described by Everett and Minkoff.[13]

Crude sodium *o*-sulphobenzaldehyde (70%; L. Light & Sons) was continuously extracted with ethanol (Soxhlet). Concentration of the extract yielded the pure salt. Sodium *p*-nitro-*o*-sulphobenzaldehyde was prepared by the oxidation of 4,4'-dinitrostilbene-2,2'-disulphonic acid with acidic permanganate. Purification was effected by alcohol-extraction of the crude sodium salt.

Sulphanilic acid (B.D.H. AnalaR) was recrystallised from water and dried at 100°.

Reaction Procedure.—Reactions were carried out in vessels immersed in a thermostat-controlled bath ($\pm 0.1°$).

(*a*) Solutions of the aldehyde (0·08M, 50 ml.) containing EDTA (0·4 mmole) and peroxyacid (0·08M, 50 ml.) at a predetermined pH, were mixed and the pH of the mixture maintained at the required level during the course of the reaction by addition of alkali. At intervals, 10 ml. aliquot parts of the reaction mixture were removed and pipetted into 0·05N-sodium arsenite (10 ml.).

The peroxyacid was estimated by titration of the excess of arsenite with 0·1N-iodine to a starch end-point, the pH being maintained close to 7 by addition of alkali. The pH of the resultant mixture was then adjusted to 4·42 and an excess of aqueous hydroxylamine hydrochloride added. The aldehyde reacts quantitatively with the hydroxylamine hydrochloride and may be estimated by the alkali required to return the pH to 4·42, neutralising the hydrochloric acid produced in the reaction.

(*b*) The pH of an aqueous solution of sulphanilic acid (0·05M, 100 ml.) containing sodium hydroxide (5 mmole) and EDTA (0·8 mmole) was adjusted to the required value and a solution of the peroxyacid (0·3M, 100 ml.) containing sodium hydroxide (5 mmole) was added. The pH of the mixture was fixed during the reaction.

At specific time intervals 5 ml. portions of the reaction mixture were removed and pipetted into beakers containing sodium arsenite solution (·2N, 10 ml.). The peroxyacid in alternate aliquot parts was determined by titrating the excess arsenite at pH 7 with standard ·2N-iodine solution using a starch indicator. The sulphanilic acid present in the remaining samples was estimated by coupling the diazotised amine with *NN*-diethyl-*N'*-1-naphthylpropane-1,3-diamine and estimating the product spectrophotometrically.[14]

In certain cases when the peroxyacids were not as soluble as peroxybenzoic acid, the concentration of reactants was reduced, and weaker reagents used for the subsequent analysis.

Product Search.—(*a*) Acidification and extraction of the reaction mixture in an experiment of the type described above, but with increased reactant concentrations, gave *ca.* 80% yield of the carboxylic acid derived from the peroxyacid. The residual aqueous liquors were reduced to small volume and passed down an ion-exchange column (Amberlite IR, 120H). Evaporation of the eluents gave a sticky solid which was identified as *o*-sulphobenzoic acid by conversion into its *S*-benzylthiouronium derivative. An 80% yield of *o*-sulphobenzoic acid was obtained.

(*b*) During the reaction of peroxybenzoic acid with sulphanilic acid at pH 5, the peroxyacid was destroyed rapidly and a deep yellow colour generated. The solution was set aside for 1 hr. and then acidified and extracted with ether. The extracts gave a 92% yield of benzoic acid. Neutralisation and evaporation of the residual solution to dryness gave a yellow solid from which crude sodium *p*-nitrobenzenesulphonate was isolated by extraction with hot ethanol. The pure salt in a 54% yield was obtained by recrystallisation from mixtures of ethyl and amyl alcohols.

Results

(*a*) The stoicheiometry of the reaction of substituted peroxybenzoic acids with sodium *o*-sulphobenzaldehyde was shown to be 1 : 1 peroxyacid : aldehyde, after allowance for the disappearance of peroxyacid from the system by its uncatalysed autodecomposition.[8] Because of this alternative reaction of the peroxyacid, the rate constants for the process could not be determined by using the standard second-order equation. Instead, the concentration of each reactant was plotted against time (Fig. 1) and the rates of disappearance of aldehyde at different times calculated by the construction of tangents to the curve using a glass rod tangentimeter.[15]

[13] Everett and Minkoff, *Trans. Faraday Soc.*, 1953, **49**, 410.
[14] Daniel, *Analyst*, 1961, **86**, 640.
[15] Wigan, *J. Sci. Instr.*, 1949, **26**, 162.

The rate of disappearance of aldehyde was taken as the rate of reaction and the rate equation

$$\text{Rate} = k_0[\text{Peroxyacid}][\text{Aldehyde}]$$

was solved at several points to give values for k_0, the second-order rate constant. The mean of these results was then taken as the value for k_0 at a particular pH. For example, the results obtained from Fig. 1 were [Time min., $k_0 \times 10^2$ l./(mole sec.)] 4, 3·33; 8, 3·31; 12, 3·15; 16, 3·19, giving a mean value of k_0 as $3·25 \times 10^{-2}$ l./(mole sec.).

Values of k_0 for the reaction of peroxybenzoic acid with sodium *o*-sulphobenzaldehyde at different pH's at 25° are plotted in Fig. 2. The limiting value of k_0 at high pH is designated k_2. In Table 1 are values of k_2 for this reaction at different temperatures from which an activation
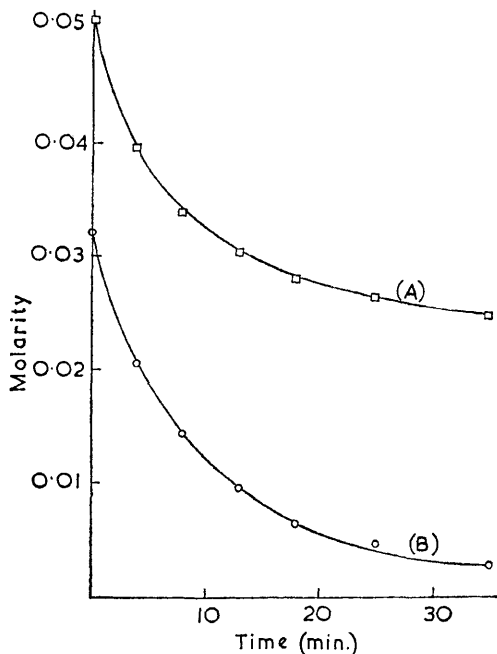

FIG. 1. Variation of the concentration of reactants with time in the reaction of sodium *o*-sulphobenzaldehyde (A) with peroxybenzoic acid (B).
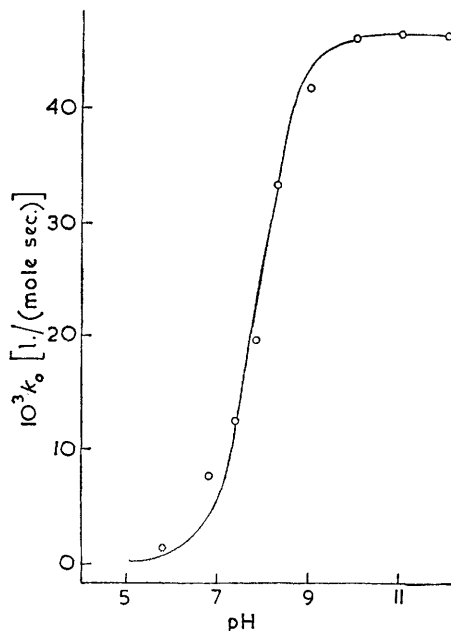
FIG. 2. Variation of the reaction rate with pH for the peroxybenzoic acid/sodium *o*-sulphobenzaldehyde reaction at 25°.

energy of 15 kcal./mole was calculated. Values for k_2 for the reaction of peroxybenzoic acid and the substituted peroxyacids with the sodium salts of 4-nitro-2-sulphobenzaldehyde and *o*-sulphobenzaldehyde, respectively, are also given in Table 2.

(b) The stoicheiometry of the reaction between peroxybenzoic acid and the sodium salt of sulphanilic acid was shown to be 3 : 1 peroxyacid to amine, after allowance for peroxyacid consumed in the accompanying decomposition process.

TABLE 1.

Aldehyde	Peroxyacid	pH	Temp.	$10^3 k_2$ [l./(mole sec.)]
o-H·O₃SC₆H₄·CHO	Ph·CO₃H	9·8	30·0°	70·0
,, ,,	,,	9·8	25·0	46·5
,,	,,	9·8	19·4	32·2
,,	*p*-NO₂·C₆H₄·CO₃H	11·3	19·4	44·0
,,	*m*-Cl·C₆H₄·CO₃H	11·6	19·4	44·0
,,	*p*-Cl·C₆H₄·CO₃H	11·7	19·4	37·1
,,	*p*-MeO·C₆H₄·CO₃H	12·0	19·4	32·6
,,	*p*-Me·C₆H₄·CO₃H	12·0	19·4	32·5
2,4-HO₃S·C₆H₃(NO₂)·CHO	Ph·CO₃H	6·9	25·0	450 (calc.)

Both amine and peroxyacid in the reaction mixture were estimated and graphs drawn of their concentrations with time. The overall rate of reaction was taken as the gradient of the tangent to the peroxyacid curve at different times (divided by 3) and rate constants, k_0', were calculated by solving the rate equation

$$\text{Rate} = k_0'[\text{Peroxyacid}][\text{Amine}]$$

This method of estimating rate of reaction was used because the accuracy of the sulphanilic acid estimation is lower than that of the iodometric determination of peroxyacid. However, the autodecomposition of the peroxyacid [8] is small but significant and the rate constants obtained in this way are of limited accuracy ($\pm 20\%$).

The reaction of peroxybenzoic acid with sulphanilic acid was studied over a range of pH at 15°. The values of k_0' obtained are given in Table 2. The percentage ionisation of the peroxyacid was calculated from a value of 8·06 for the pK at 15°. The reaction of substituted peroxybenzoic acids with sulphanilic acid at 15° and pH 9·0 was studied and the values obtained for k_0' are recorded in Table 3.

TABLE 2.

pH	8·9	9·0	9·15	9·3	9·6	10·0
$10^2 k_0'$ [l.(mole sec.)]	1·00	0·74	0·56	0·37	0·27	0·11
Ionisation (%)	87·4	89·7	92·5	94·5	97·2	98·9

DISCUSSION

Reaction of Peroxybenzoic Acids with Sodium o-Sulphobenzaldehyde.—The 1 : 1 stoicheiometry of the reaction of peroxybenzoic acids with sodium o-sulphobenzaldehyde and the reproducibility of the second-order rate constants k_0 at a single pH and different initial reactant concentrations confirmed that the reaction is of first order with respect to each reagent. The variation of k_0 with pH for the peroxybenzoic acid–sodium o-sulphobenzaldehyde reaction shows that the peroxybenzoate anion is the reactive species. The experimental values for k_0 on Fig. 2 are superimposed on the theoretical curve calculated assuming that rate is proportional to anion concentration, with a rate constant of $4·7 \times 10^{-2}$ l./mole sec. at 100% ionisation and a pK for peroxybenzoic acid at 25° of 7·78.

It is probable, therefore, that the first step in the reaction mechanism is the nucleophilic attack of the anion on the carbonyl carbon of the aldehyde. The nucleophilicity of peroxyanions has been demonstrated by Jencks and Carriuolo [16] and Wiberg.[17] The nucleophilic properties of peroxycarboxylate anions, in particular, are apparent in the reaction of the sodium salt of peroxyacids with esters [18,19] yielding peroxides. It is also significant that the peroxycarboxylate anion is concerned in the rate-determining step of the decomposition of peroxyacids.[8]

The peroxy intermediate formed by the reaction of the peroxycarboxylate anion with aldehyde may decompose to give the observed products, benzoic acid and o-sulphobenzoic acid, *via* an intramolecularly hydrogen-bonded form.
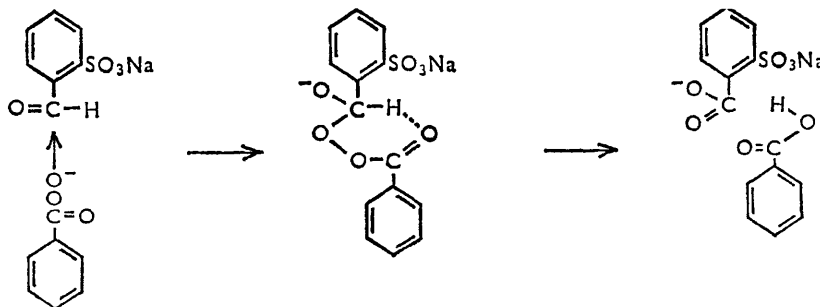
[16] Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.
[17] Wiberg, *J. Amer. Chem. Soc.*, 1955, **77**, 2519.
[18] Swain, Stockmeyer, and Clark, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.
[19] Cooper, *J.*, 1951, 3106.

This type of cyclic intermediate has been proposed by Syrkin and Moiseev [20] for reactions and rearrangements of peroxy species in non-aqueous solution and adopted for aqueous systems.[8] Baddeley [21] has suggested that reactions of the hydroperoxide anion may proceed by similar mechanisms.

Peroxyacids containing electron-withdrawing groups react at a higher rate than peroxybenzoic acid while electron-donating groups have little effect (Table 1). The step containing the nucleophilic attack of the percarboxylate anion cannot, therefore, be rate determining as electron-withdrawing groups in the peroxyacid would retard this step. The most probable explanation is that the intermediate is formed by an equilibrium process (lying to the left) and that breakdown to the products is slow. When a small, steady concentration of the intermediate has formed, the kinetic situation will be as follows:

$$RCO_3^- + \text{Aldehyde} \underset{k}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate} \xrightarrow{k_3} \text{Products}$$
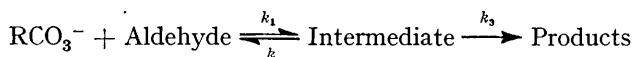
$$\text{Rate of reaction} = k_3 \text{ [Intermediate]}$$

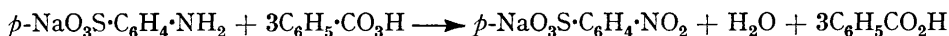$$[\text{Intermediate}] = \frac{k_1}{k} [RCO_3^-][\text{Aldehyde}]$$

Hence

$$\text{Rate} = \frac{k_3 k_1}{k} [RCO_3^-][\text{Aldehyde}]$$

Our rate constant k_2 is, therefore, equal to $k_1 k_3 / k$.

The effects of substituents in the peroxyacid nucleus may now be interpreted. The electronegative group, *e.g.*, *m*-chloro, lowers the nucleophilicity of the percarboxylate anion and will affect the equilibrium, but the resultant intermediate will be less stable, and the reaction will proceed faster, *i.e.*, k_3 will be larger, because the electronegative substituent will enable the homolysis of the O–O bond to proceed more easily. With an electron-donating substituent, the nucleophilicity of the anion will be increased, but the O–O bond in the intermediate will be strengthened. These effects must be of comparable size, for the overall reaction rate is affected only marginally. Support for this mechanism derives from the observation that sodium 4-nitro-2-sulphobenzaldehyde reacts with peroxyacids much faster than does sodium *o*-sulphobenzaldehyde. The nitro group will have the effect of increasing both k_1 and k_3 with a large overall increase in reaction rate.

This type of mechanism, with the intermediate state attained through an equilibrium process, was proposed to explain the substituent effects observed in the reaction of a series of substituent benzaldehydes with peroxybenzoic acid in benzene solution,[22] though in that case, the initial step was the electrophilic addition of the un-ionised peroxyacid across the C=O bond of the carbonyl group.

Reaction of Peroxybenzoic Acids with Sodium Sulphanilate.—As the overall stoicheiometry of the reaction of peroxybenzoic acid with sodium sulphanilate in aqueous alkali was shown to be 3 : 1 peroxyacid to amine and sodium *p*-nitrobenzenesulphonate and benzoic acid were the only isolable reaction products, the main process must be as follows:

$$p\text{-}NaO_3S{\cdot}C_6H_4{\cdot}NH_2 + 3C_6H_5{\cdot}CO_3H \longrightarrow p\text{-}NaO_3S{\cdot}C_6H_4{\cdot}NO_2 + H_2O + 3C_6H_5CO_2H$$

In presence of an excess of amine, the peroxyacid disappeared by a pseudo-first-order reaction and the good reproducibility of second-order rate constants calculated for a range of reactant concentrations confirmed that the process was first order with respect to each reagent.

The variation of the rate constant k_0' for the peroxybenzoic acid–sulphanilic acid reaction with pH and degree of ionisation (see Table 2) demonstrates clearly that the

[20] Syrkin and Moiseev, *Uspekhi Khim.*, 1960, **29**, 425.
[21] Baddeley, *Ann. Reports*, 1955, **52**, 150.
[22] Ogata, Tabushi, and Akimoto, *J. Org. Chem.*, 1961, **26**, 4803.

un-ionised peroxyacid is the reactive species. By extrapolation of the straight line plot of k_0' against degree of ionisation a value of $7\cdot7 \times 10^{-2}$ l./mole sec. for k_2', the real rate constant for the reaction of the un-ionised peroxyacid with sulphanilic acid at 15°, was derived. It was found that electron-withdrawing groups increase k_2' while electron-donating substituents reduce it (Table 3). The peroxyacid is, therefore, acting electrophilically. This type of behaviour was noted by Ibne-Rasa, Lauro, and Edwards who studied the oxidation of amines [23] and nitroso-compounds [24] by aliphatic peroxyacids in ethanolic and aqueous ethanolic solution. They also reported [23] an acceleration in rates of reaction on increasing the amount of water in the system.

In the present work it has been demonstrated that the reactivity of the un-ionised peroxyacids with amines is many orders of ten greater than that of the peroxy anion. This

TABLE 3.

Substituted peroxybenzoic acid	$10^2 k_0'$ at pH 9·0 [l./(mole. sec.)]	pK at 15°	Ionisation (%) of peroxyacid	$10 k_2'$ (calc.) [l./(mole. sec.)]
p-NO$_2$	0·60	7·36	97·8	2·71
m-Cl	0·48	7·71	95·1	0·98
p-Cl	0·80	7·90	92·7	1·10
Unsubst.	0·73	8·06	89·7	0·77
p-Me	0·43	8·22	85·8	0·30
p-MeO	0·33	8·29	83·8	0·20

point has not been made clear previously, for no variation of reaction rates with pH in these systems has been reported.

The mechanism of the reactions of peroxyacids with organic substrates in non-aqueous systems is now understood.[3-7] A cyclic transition state is achieved *via* the electrophilic attack of the peroxyacid on the electron-rich centre in the organic compounds, viz.: [3]
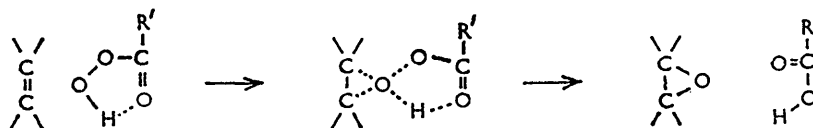
Ibne-Rasa and Edwards [23] have explained the marked influence of solvents on reaction rate of peroxyacids in part-aqueous systems in terms of participation of a solvent molecule in this type of transition state. It is suggested that the reaction under study here proceeds in a similar manner.
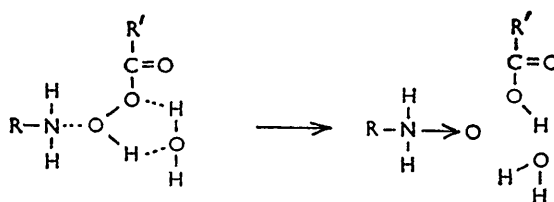
The ensuing steps of the process, involving successive formation of nitroso- and nitro-compounds, are rapid and the overall mechanism is therefore:
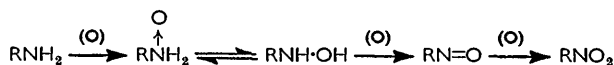
It is thought that the deep yellow colour which the reaction solution develops is due to the formation in small amounts of azo- and azoxy-compounds by condensation of these inter-mediates.

[23] Ibne-Rasa and Edwards, *J. Amer. Chem. Soc.*, 1962, **84**, 763.
[24] Ibne-Rasa, Lauro, and Edwards, *J. Amer. Chem. Soc.*, 1963, **85**, 1165.

Thus we have shown that, in aqueous alkaline solution, peroxyacids may react electrophilically or nucleophilically with organic substrates, in contrast to the solely electrophilic properties of peroxyacids in non-aqueous media.   Application of the nucleophilic properties of peroxyacids in aqueous alkaline media should extend their use as oxidising agents in synthetic organic chemistry.[1]

PROCTER AND GAMBLE LTD., BASIC RESEARCH DEPT., WHITLEY ROAD,
LONGBENTON, NEWCASTLE UPON TYNE 12.   [*Received, February 12th*, 1964.]