Tetrahedron. Vol. 26, pp. 2519 to 2526. Pergamon Press 1970. Printed in Great Britain

DECOMPOSITION OF SODIUM PEROXYBENZOATE IN SODIUM HYDROXIDE SOLUTION

K. AKIBA and O. SIMAMURA*

Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo, Japan

(*Received in Japan* 13 *October* 1969; *Received in the UK for publication* 2 *February* 1970)

Abstract—Sodium peroxybenzoate decomposes to give sodium benzoate and oxygen in dilute aqueous sodium hydroxide. In 1N NaOH at 0°, however, sodium peroxybenzoate is hydrolyzed to yield sodium benzoate and hydrogen peroxide without evolution of oxygen. In 10^{-3}N NaOH at 0°, decomposition of sodium peroxybenzoate itself is very slow, but it reacts with undissociated hydrogen peroxide to give oxygen and sodium benzoate. In alkaline solutions of intermediate concentration, these two reactions occur side by side, the hydrogen peroxide initially produced by hydrolysis reacting with the peroxybenzoate anion to give oxygen.

RECENTLY it was noticed that in aqueous alkali peroxybenzoic acid decomposes quickly to give benzoic acid and oxygen. The amount of oxygen evolved varies with the concentration of the alkali and does not obey the simple stoichiometry of one molecule of oxygen from two molecules of sodium peroxybenzoate. This paper deals with the mechanism of this decomposition.

Some peroxyacids have been shown to decompose rapidly in aqueous alkaline solution when the pH is equal to the pK_a value, i.e., when they are 50% dissociated.[1-3] The decomposition of peroxybenzoic acid was investigated in aqueous alkali of pH ranging from 6·6 to 9·0,[1,2] in which an appreciable amount of peroxybenzoic acid exists in the undissociated form, its pK_a being 8·0.[4] Under these conditions the reaction is complex and in addition to oxygen, a small quantity of benzoyl peroxide is formed.[1,2] In the present investigation, the results of which were preliminarily communicated elsewhere,[5] alkaline solutions of pH's higher than 11 were used. In such solutions sodium peroxybenzoate is almost completely dissociated.

The rate of the decomposition of sodium peroxybenzoate in aqueous sodium hydroxide was followed by iodometry,[6] and pseudo-unimolecular rate constants (k_1) were calculated using the titres up to 70% of the decomposition. Typical runs are shown in Fig 1 and the results are tabulated in Table 1. The rate of decomposition did not vary when experiments were carried out under either nitrogen, air or oxygen, excluding thus the possibility of a homolytic mechanism.

The pseudo-unimolecular rate constant decreases with the concentration of the hydroxide ion used, but the dependency is not proportional as easily seen by comparing the apparent second order rate constants (k_2) obtained by dividing the pseudo-unimolecular constants by the concentrations of the hydroxide ion. This fact suggests that the decomposition of sodium peroxybenzoate is of complex nature as has been adumbrated by the observation that the amount of oxygen evolved varies with the alkalinity of reacting solutions. Further, Fig 1 shows that the rate of decomposition

---

* To whom correspondence should be addressed.

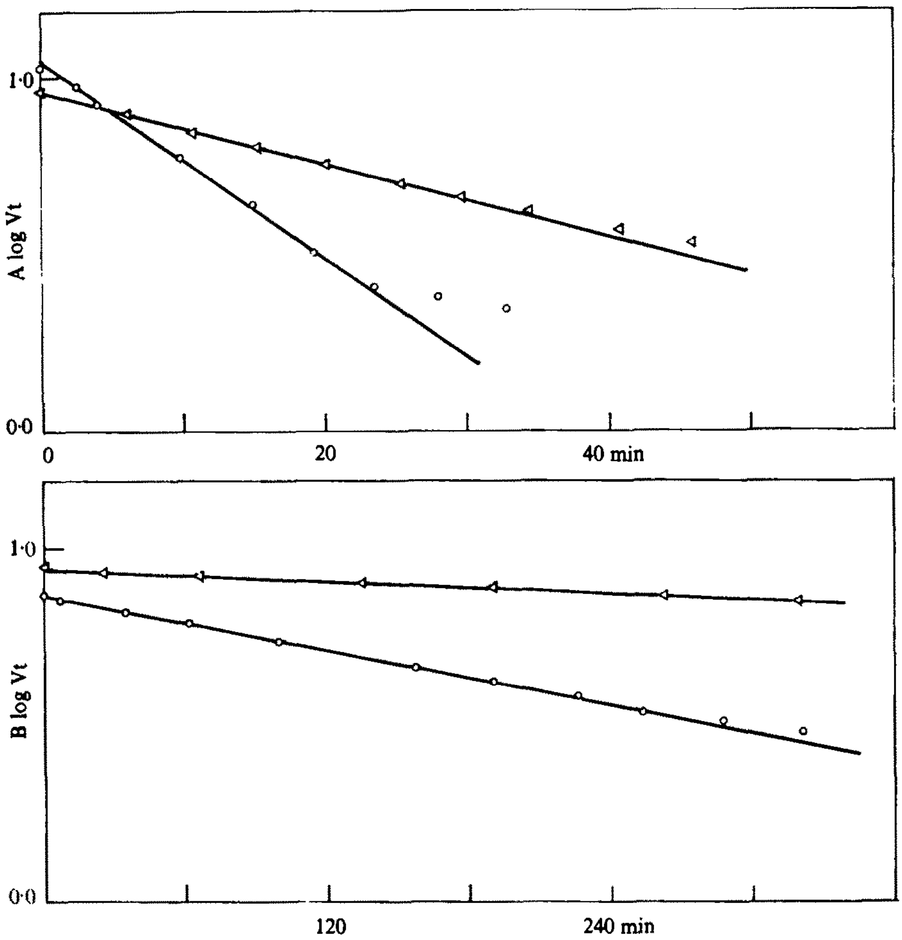


Fig 1. Decomposition of sodium peroxybenzoate in NaOHaq at 30·0°
A -○- 1N NaOH, -◁- 0·5N NaOH
B -○- 10^{-1}N NaOH, -△- 10^{-2}N NaOH
V_t represents volume (ml) of a standard sodium thiosulphate solution (0·003086N) consumed for 2 ml of a reacting solution

decreased after about 70% of sodium peroxybenzoate had reacted owing to formation of hydrogen peroxide.

In 1N or 0·5N NaOH at 0°, sodium peroxybenzoate decomposed without evolution of oxygen during an initial period of 2 or 3 hr. In these experiments, both sodium peroxybenzoate and hydrogen peroxide were separately estimated by iodometry and titration with a standard ceric salt solution.[7] The results showed that the amount of peroxybenzoate decomposed was equal to the hydrogen peroxide produced (Table 2), indicating that only hydrolysis had taken place.

Therefore, k_1 or k_2 for the decomposition in 1N NaOH corresponds to the alkaline hydrolysis (k_{hydr}) of sodium peroxybenzoate:

$$PhC(:O)OO^- + OH^- \xrightarrow{k_{hydr}} PhCOO^- + HOO^- \quad (1)$$

TABLE 1. RATE CONSTANTS, k_1 (SEC^{-1}), OF DECOMPOSITION OF SODIUM PEROXYBENZOATE

	NaOH			
Temp	1N	0·5N	10^{-1}N	10^{-2}N
30°	$1·10 \times 10^{-3}$	$4·32 \times 10^{-4}$	$5·17 \times 10^{-5}$	$1·28 \times 10^{-5}$
	1·14	4·13	5·03	1·31
20°	$3·60 \times 10^{-4}$		$2·38 \times 10^{-5}$	$4·48 \times 10^{-6}$
	3·65		2·48	4·25
0°	$3·00 \times 10^{-5}$		*	*
	2·83			

Initial concentration of $PhCO_3Na$, ca. 10^{-2} M

* The decomposition is too slow to be measured.

A similar hydrolysis of peroxyacetic acid to acetic acid and hydrogen peroxide has been reported.[8]

The Arrhenius plot of rate constants k_{hydr} in 1N NaOH (Fig. 2) gives the activation energy for the hydrolysis as 17·0 kcal/mol.

An alternative mechanism, compatible with the kinetic results, is the donation of an O atom from a peroxybenzoate anion to a hydroxide ion:

$$PhC(:O)OO^- + \overset{*}{O}H^- \rightarrow PhC(:O)O^- + H\overset{*}{O}O^- \tag{2}$$

This possibility was excluded by experiments in which sodium peroxybenzoate was

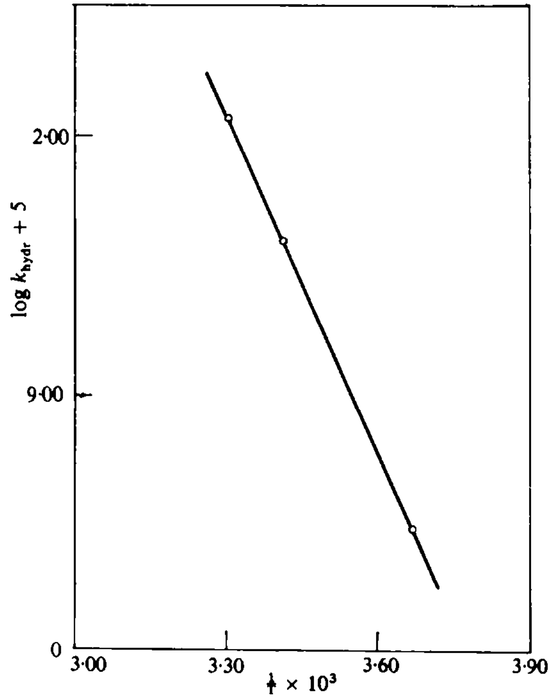


FIG 2. The Arrhenius plot of rate constants, k_{hydr}, for hydrolysis of sodium peroxybenzoate by the hydroxide ion.

$k_{hydr} = 1·74 \times 10^9 \cdot \exp(-17{,}000/RT)$ l mol^{-1} sec^{-1}

allowed to decompose in a solution of sodium hydroxide in water enriched with ^{18}O (1·57%) for about 20 hr at 0°; the ^{18}O content in the oxygen liberated by adding ceric sulphate to the reaction mixture was found to be normal (^{18}O, 0·205%). Separate experiments showed that no exchange of oxygen takes place between hydrogen peroxide and the hydroxide ion under the present experimental conditions, thus confirming earlier results.[9] Therefore, hydrolysis to benzoic acid and hydrogen peroxide is the initial step in the decomposition of sodium peroxybenzoate in alkaline solution.

Since the hydrolysis was rapid in concentrated alkaline solution without oxygen being evolved, and as a decrease in alkalinity caused the evolution of oxygen, the latter was probably produced by the action of sodium peroxybenzoate on undissociated molecules of the hydrogen peroxide liberated. This inference was borne out by experiments. Indeed in a 10^{-3}N NaOH sodium peroxybenzoate reacted with an equivalent amount of hydrogen peroxide at 0° according to the following equation:

TABLE 2. A TYPICAL KINETIC RUN OF THE DECOMPOSITION OF SODIUM PEROXYBENZOATE IN 1N NaOH AT 0°

Time min	$PhCO_3Na$ 10^{-3} M	HOOH 10^{-3} M	$PhCO_3Na$ + HOOH 10^{-3} M	$k_1 \times 10^5$ sec^{-1}
0	12·66	0·30	12·96	—
15	12·54	0·75	13·29	1·05
45	11·49	1·14	12·53	3·58
103	10·50	2·37	12·87	3·01
168	9·48	3·33	12·81	2·87
223	8·55	4·26	12·81	2·93
291	7·38	5·31	12·69	3·09
410	6·00	6·63	12·63	3·03

First order rate constants (k_1) were calculated using the concentrations of sodium peroxybenzoate.

$$PhC(:O)OONa + H_2O_2 \rightarrow PhC(:O)ONa + O_2 + H_2O \qquad (3)$$

On the other hand in a 1N NaOH at 0°, in the presence of an excess of hydrogen peroxide, sodium peroxybenzoate was hydrolyzed almost completely to hydrogen peroxide, and the amount of oxygen evolved, measured after a reaction time of 24 hr, was very small, corresponding to 5·6% of the peroxybenzoate used. This difference is explained by the fact that in 10^{-3}N NaOH nearly 90% of hydrogen peroxide exists in the undissociated form ready to react with the peroxybenzoate anion, whereas in 1N NaOH the concentration of the undissociated form is too low for the reaction with the peroxybenzoate to proceed measurably fast. In solutions of intermediate alkalinity, evolution of oxygen was slower than in 10^{-3}N aqueous alkali.

In addition, both sodium peroxybenzoate and hydrogen peroxide decompose very slowly (less than 2% in 7 hr at 0°) in 10^{-3}N or 10^{-2}N aqueous sodium hydroxide, and peroxybenzoic acid and hydrogen peroxide do not react in aqueous methanol.

Further evidence for reaction (3) is afforded by kinetic measurements of the decrease of both sodium peroxybenzoate and hydrogen peroxide in 10^{-3}N and 10^{-2}N sodium hydroxide solutions at 0°; typical runs are shown in Table 3 and the results are listed in Table 4. Although in 10^{-3}N NaOH one mole of hydrogen

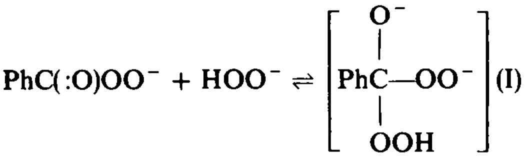
TABLE 3. TYPICAL KINETIC RUNS OF THE REACTION BETWEEN SODIUM PEROXYBENZOATE AND HYDROGEN PEROXIDE AT 0°

Time min	$PhCO_3Na$ 10^{-3} M	HOOH 10^{-3} M	$k_{dec}^{obs} \times 10^2$ l mol^{-1} sec^{-1}
	A, in 10^{-3}N NaOH		
0	20·34	8·43	—
6	19·14	7·32	1·86
13	18·39	6·48	1·76
20	17·43	5·55	1·82
30	16·95	4·74	1·83
36	16·29	4·35	1·71
42	15·57	3·81	1·76
49	15·42	3·33	1·86
57	15·03	2·88	1·93
72	14·22	2·31	1·82
83	13·89	1·86	1·90
	B, in 10^{-2} N NaOH		
0	14·25	9·96	—
9	14·01	9·63	6·34
37	13·56	9·06	4·51
106	12·63	8·04	3·41
140	12·33	7·62	3·22
180	12·03	7·23	3·25
217	11·28	6·69	3·43
295	10·83	6·12	3·14
356	10·26	5·61	3·00
422	9·99	5·10	3·12

TABLE 4. RATE CONSTANTS OF THE REACTION BETWEEN SODIUM PEROXYBENZOATE AND HYDROGEN PEROXIDE AT 0°

Run in	Initial concentration $PhCO_3Na$ M	Initial concentration HOOH M	Ratio of reactants consumed, $\frac{\Delta \text{HOOH}}{\Delta \text{PhCO}_3\text{Na}}$		$k_{dec}^{obs} \times 10^2$ l mol^{-1} sec^{-1}
10^{-3}N NaOH	0·0203	0·00844	1·02		1·83
	0·0171	0·00853	1·03		1·68
	0·0182	0·00853	1·01		1·98
				mean	1·83
10^{-2}N NaOH	0·0142	0·00997	1·22		0·322
	0·0140	0·00990	1·26		0·323
	0·0183	0·0107	1·47		0·267
	0·0158	0·0101	1·19		0·368
				mean	0·320

peroxide was consumed for one mole of sodium peroxybenzoate, in 10^{-2}N NaOH about 1·25 moles of hydrogen peroxide was consumed per mole of the peroxybenzoate throughout the reaction. A possible explanation for this observation may be as follows: Nucleophilic attack on a peroxybenzoate anion by a hydrogen peroxide anion may produce an intermediate (I), and this may either revert to the reactants causing exchange of HO_2^- or rearrange to give a phenoxycarbonylperoxy anion (II) as shown in the following scheme:



$$PhC(:O)OO^- + HOO^- \rightleftharpoons \left[\begin{array}{c} O^- \\ | \\ PhC—OO^- \\ | \\ OOH \end{array}\right] (I)$$

$$(I) \rightarrow PhOC(:O)OO^- \ (II) + OH^-$$

$$(II) + HOOH \rightarrow PhOCOO^- + O_2 + H_2O$$

The phenoxycarbonylperoxy anion would behave in a manner similar to the peroxybenzoate anion in the titration and also in the reaction with hydrogen peroxide. The exchange of a peroxy group was demonstrated by experiments using sodium peroxybenzoate-(peroxy^{18}O).[10] After the usual working-up, a small amount of phenol was isolated as 2,4,6-tribromophenol. This indicates the formation of monophenyl carbonate anions, which is known to yield phenol easily in neutral or acidic solution.[11]

In view of this complication, the rate constant obtained for the reaction in 10^{-3}N NaOH is a more reliable estimate than that in 10^{-2}N NaOH. Since the pH of the reacting solution in 10^{-3}N NaOH was found to be 10·6, the pK_a value of 11·6 for the dissociation of H_2O_2[12] gives the fraction of undissociated hydrogen peroxide to be 0·946 in 10^{-3}N NaOH. The observed second order rate constant $k_{dec}^{obs} = 1{\cdot}83 \times 10^{-2}$ should accordingly be corrected for this fraction, giving $k_{dec} = 1{\cdot}83 \times 10^{-2}/0{\cdot}946 = 1{\cdot}94 \times 10^{-2}$ l mol^{-1} sec^{-1}.

Thus, the overall mechanism for the decomposition of sodium peroxybenzoate in alkaline solution is represented by a sequence of the following reactions:

$$PhC(:O)OO^- + HO^- \xrightarrow{k_{hydr}} PhC(:O)O^- + HOO^- \qquad (1)$$

$$HOO^- + H_2O \overset{K}{\rightleftharpoons} HOOH + HO^- \qquad (4)$$

$$PhC(:O)OO^- + HOOH \xrightarrow{k_{dec}} PhC(:O)O^- + O_2 + H_2O \qquad (3)$$

and the rate of the decomposition of sodium peroxybenzoate therefore consists of two terms corresponding to the hydrolysis and the reaction with hydrogen peroxide:

$$\begin{aligned} &-d[PhCO_3^-]/dt \\ &\quad = k_{hydr}[PhCO_3^-][HO^-] + k_{dec}[PhCO_3^-][H_2O_2] \\ &\quad = k_{hydr}[PhCO_3^-][HO^-] + k_{dec}/(1 + [HO^-]/K[H_2O]) \cdot [PhCO_3^-](H_2O_2) \qquad (5) \end{aligned}$$

where (H_2O_2) represents the analytical concentration of hydrogen peroxide, i.e., $[HO_2^-] + [H_2O_2]$.

The relative importance of the hydrolysis *versus* the reaction with hydrogen peroxide depends on the concentration of hydroxide ions as shown in Table 5, which lists the constant factors in Eq. (5) calculated by using the experimental values of the reaction rate constants and the pK_a of 11·6 for hydrogen peroxide. Since the value for (H_2O_2) is always less than 10^{-2}M, i.e., the initial concentration of sodium peroxybenzoate, it is understandable that, when $[HO^-] = 1$, the hydrolysis takes place without evolution of oxygen. When $[HO^-] = 10^{-2}$ or 10^{-1}, although the initial concentration of hydrogen peroxide is negligible, the evolution of oxygen sets in as the hydrolysis gives rise to hydrogen peroxide.

TABLE 5. VALUES FOR THE CONSTANT FACTORS IN EQ. (5) AT 0°

$[HO^-]$	$k_{hydr}[HO^-]$	$k_{dec}/(1 + [HO^-]/K[H_2O])$
1	$2{\cdot}92 \times 10^{-5}$	$7{\cdot}70 \times 10^{-5}$
10^{-1}	$2{\cdot}92 \times 10^{-6}$	$7{\cdot}43 \times 10^{-4}$
10^{-2}	$2{\cdot}92 \times 10^{-7}$	$5{\cdot}53 \times 10^{-3}$

EXPERIMENTAL

Materials. Peroxybenzoic acid was prepared from benzoyl peroxide and NaOMe according to Braun's procedure[13] as modified by Kolthoff *et al.*[14] CH_2Cl_2 was used to extract peroxybenzoic acid, and the extract was dried over Na_2SO_4 and evaporated in vacuum. Peroxybenzoic acid was finally purified by sublimation in vacuum.

NaOH (100 g) recrystallized from EtOH was dissolved in de-ionized water (100 ml) and the soln allowed to stand for more than 2 weeks to precipitate Na_2CO_3 (Sørensen's solution). Portions of this soln were diluted with de-ionized water to give solutions of required concentrations, which were used as solvents for kinetic study.

AcOH was refluxed with $KMnO_4$ for several hr and distilled. Commercial H_2O_2 (30%, stabilizer free) was used without purification. N_2 was freed from O_2 according to Fieser's directions.[15]

De-ionized water was prepared by passing distilled water through a mixed-bed of cation- and anion-exchangers (Amberlite IR-120 and IRA-410).

Preparation of sodium peroxybenzoate

(a) Peroxybenzoic acid in CH_2Cl_2 (0·4 M, 3·00 ml) was added slowly to 1N NaOH in abs EtOH (prepared by dissolving Sørensen's soln in abs EtOH) at 0° (mole ratio of NaOH to peroxybenzoic acid, 1·1–1·2). Then a small amount of CH_2Cl_2 or light petroleum (ca. 30 ml) was added to complete precipitation of sodium peroxybenzoate. The ppt was collected on a sintered glass filter under a stream of dry air, which was freed from CO_2, washed with EtOH (ca. 15 ml) and then dried. The sodium peroxybenzoate thus prepared (the active O content, 60–75% of the theoretical) was dissolved in an NaOH aq. If excess peroxybenzoic acid was used, part of the sodium peroxybenzoate formed reacted rapidly with the remaining free peroxybenzoic acid, producing a small amount of benzoyl peroxide.[1,2] This is also true for procedure (b) described below. Solns of sodium peroxybenzoate were freshly prepared before each experiment.

(b) Peroxybenzoic acid in CH_2Cl_2 (0·4 M, 3·0 ml) was added slowly to 1N NaOH at 0° (mole ratio of NaOH to peroxybenzoic acid, 1·1–1·2). Removal of the CH_2Cl_2 by suction with a water-jet aspirator gave a concentrated aqueous soln of sodium peroxybenzoate. This soln was diluted with NaOHaq to give a soln of the peroxybenzoate of desired concentration.

Procedure (b) was adopted only in the experiments summarized in Table 1, but for other experiments procedure (a) was used throughout.

Selective titration of a mixture of peroxybenzoic acid and hydrogen peroxide. A sample taken in a 1–3N AcOH (ca. 30 ml) kept at ±0° by ice cooling was titrated first for H_2O_2 with a standard ceric sulphate (0·03002N) using ferroin as an indicator, and then for peroxybenzoic acid by iodometry.[7] Analysis of mixtures of known amount of both peroxides gave values slightly lower than the theoretical (less than 1% for H_2O_2 and less than 1·5% for peroxybenzoic acid).

Kinetic measurements of decomposition of sodium peroxybenzoate in aqueous sodium hydroxide. Aliquots (2·00 ml) were withdrawn at intervals from a thermostated reacting soln and peroxybenzoic acid was titrated with a standard $Na_2S_2O_3$ (0·003086N),[6] or peroxybenzoic acid and H_2O_2 were fractionally titrated as mentioned above.

Tolerably reproducible results were obtained when the following procedure was adopted: A reaction vessel was washed successively with a conc methanolic soln of KOH, conc HNO_3 and water. It was then filled with NaOHaq containing peroxybenzoic acid and left overnight at room temp, and finally it was thoroughly washed with de-ionized water and dried.

Separate experiments showed that even traces of heavy metals ions, such as Cu, Co, and Fe, accelerate the decomposition, and therefore de-ionized water was used throughout.

Kinetic measurements of decomposition of sodium peroxybenzoate in the presence of hydrogen peroxide. A mixture was prepared by pipetting an alkaline soln of H_2O_2 into a known volume of alkaline aqueous sodium peroxybenzoate at 0°, and aliquots (5·00 ml, 0·01–0·02 M) withdrawn at intervals were titrated fractionally for H_2O_2 and sodium peroxybenzoate. Typical runs are shown in Table 4.

pH of reaction mixtures. In a closed vessel, change in the pH value of a reaction mixture during a kinetic run was negligible even with a 10^{-2}N or 10^{-3}N NaOH. The presence of H_2O_2, however, lowered the pH value, since pK_a of H_2O_2 is 11·6. The actual value of pH of mixtures was found to be 11·81 in 10^{-2}N and 10·58 in 10^{-3}N NaOH.

Estimation of oxygen evolved from mixtures of hydrogen peroxide and sodium peroxybenzoate. In a tube of a known volume, cleaned as described, a soln (2·00 ml) of H_2O_2 of appropriate concentration in NaOHaq was chilled with dry-ice–EtOH. The air above the soln was evacuated thoroughly with alternate chilling and thawing, then a sodium peroxybenzoate soln (2·00 ml) of appropriate concentration in NaOHaq was pipetted on top of the frozen mass. The mixture was chilled again, and the tube evacuated. It was then filled with N_2, sealed off and allowed to stand in an ice–water bath for 24 hr. The evolved O_2 was estimated with a mass-spectrometer (Model 21–103A, Consolidated Engineering Corporation).

Decomposition of sodium peroxybenzoate in water enriched in ^{18}O. Sodium peroxybenzoate was dissolved in 1·047N NaOH ($H_2{}^{18}O$, ^{18}O content, 1·57%) to yield a ca. 0·01 M or 0·06 M soln. The soln (5·00 ml) in a tube was kept for about 20 hr at 0°; then the air above the soln was evacuated with alternate chilling and thawing of the contents. A ceric sulphate soln (0·1 N, 5·00 ml), which was 3N in H_2SO_4, was then added to the solidified mass. After the whole mixture was chilled, the tube was sealed under an atmosphere of N_2 and left at room temp. The ^{18}O content in the oxygen formed was estimated by mass-spectrometry.

REFERENCES

[1] W. Kirmse and L. Horner, *Chem. Ber.* **89**, 836 (1956)

[2] J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.* **58**, 1846 (1962)

[3] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *Ibid.* **85**, 2263 (1963)

[4] R. Wolf, *Bull. Soc. Chim. Fr.* **21**, 644 (1954)

[5] K. Akiba and O. Simamura, *Chem. & Ind.* 705 (1964)

[6] D. Swern, *Organic Reactions* Vol. VII: p. 392, Wiley, New York (1953)

[7] F. P. Greenspan and D. G. MacKellar, *Analyt. Chem.* **20**, 1061 (1948)

[8] J. D'Ans and J. Mattner, *Angew. Chem.* **63**, 368 (1951)

[9] E. R. S. Winter and H. V. A. Briscoe, *J. Am. Chem. Soc.* **73**, 496 (1951); C. A. Bunton and D. R. Llewellyn, *Research* **5**, 142 (1952); A. E. Cahill and H. Taube, *J. Am. Chem. Soc.* **74**, 2312 (1952); M. Anbar, *Ibid.* **83**, 2031 (1961)

[10] K. Akiba and O. Simamura, *Tetrahedron* **26**, 3527 (1970)

[11] R. Schmidt, *J. Prakt. Chem.* **31**, 406 (1885)

[12] A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.* **49**, 410 (1953)

[13] G. Braun, *Organic Syntheses* Coll. Vol. I, p. 431, Wiley, New York (1951)

[14] I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.* **2**, 199 (1947)

[15] L. F. Fieser, *Experiments in Organic Chemistry* (3rd Edition) p. 299, Heath, Boston (1955)