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THE MECHANISM OF THE REACTION BETWEEN SODIUM PEROXYBENZOATE AND HYDROGEN PEROXIDE IN ALKALINE SOLUTIONS

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Abstract—Sodium peroxybenzoate reacts with hydrogen peroxide to give sodium benzoate and oxygen:

$$PhC(:O)OO^- + H_2O_2 \longrightarrow PhCOO^- + O_2$$

The O_2 originates from a molecule of hydrogen peroxide in experiments using sodium peroxybenzoate labelled with ^{18}O at the peroxidic O atoms.

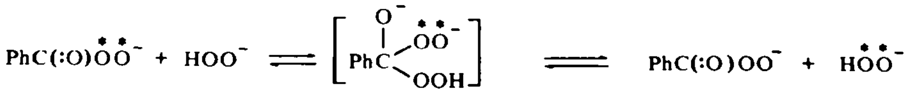
Peroxybenzoic acid decomposes in aqueous alkali of certain concentrations to give benzoic acid and oxygen according to the following sequence:[1,2]

$$PhC(:O)OO^- + OH^- \longrightarrow PhCOO^- + HO_2^- \quad (1)$$

$$HO_2^- + H_2O \rightleftharpoons H_2O_2 + OH^- \quad (2)$$

$$PhC(:O)OO^- + H_2O_2 \longrightarrow PhCOO^- + O_2 + H_2O \quad (3)$$

In order to determine the origin of the oxygen evolved in reaction (3), sodium peroxybenzoate-(peroxy-^{18}O) (^{18}O content, 1·401%) was allowed to react with hydrogen peroxide (^{18}O content, 0·205%, natural abundance) in aqueous sodium hydroxide under a nitrogen atmosphere, and the evolved oxygen was analyzed by mass-spectrometry (see Table 1). Oxygen-18 contents were found to be 0·56% (in 10^{-2}N NaOH) and 0·66% (in 10^{-3}N NaOH) when the molar ratio of hydrogen peroxide to the peroxybenzoate was about 1·3, and 0·24% when this ratio was increased to 13. According to whether the oxygen originates solely from the peroxybenzoate anion, or solely from hydrogen peroxide, or from a peroxybenzoate anion and hydrogen peroxide, each donating one atom to form one molecule of oxygen, the oxygen-18 content should be 1·401, 0·205, and 0·803, respectively. As values found for oxygen-18 content cannot be accounted for by any of these three possibilities, there is probably a rapid exchange equilibration between the two reactants in dissociated forms:



$$PhC(:O)\overset{*}{O}\overset{*}{O}^- + HOO^- \rightleftharpoons \left[PhC\begin{matrix} O^- \\ \overset{*}{O}\overset{*}{O}^- \\ OOH \end{matrix}\right] \rightleftharpoons PhC(:O)OO^- + H\overset{*}{O}\overset{*}{O}^-$$

Such exchange is not unreasonable in view of facile nucleophilic attack on the ester-carbonyl group by the hydrogen peroxide anion.[3] Since in all the experiments, the oxygen-18 content was found to be less than that calculated on the assumption that the

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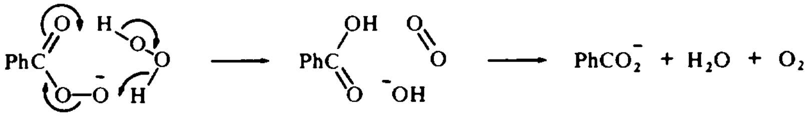
exchange equilibration takes place very rapidly and is complete before any oxygen evolution sets in, this indicates that the oxygen is derived solely from hydrogen peroxide.

In order to exclude the complication due to the exchange equilibrium, methanol was used as a reaction medium. In fact, in methanol without any added alkali, one mole of sodium peroxybenzoate reacts with one mole of hydrogen peroxide to yield oxygen (about 90% of the theoretical). Table 2 shows the results of experiments with sodium peroxybenzoate labelled with oxygen-18 (^{18}O content, 1·455%) and hydrogen peroxide (^{18}O content, 0·205%, natural abundance) in anhydrous methanol under a nitrogen atmosphere. The oxygen-18 content of oxygen evolved ranged from 0·20 to 0·24% when the molar ratio of the two reactants was varied ten fold. This finding unequivocally demonstrates that the oxygen evolves exclusively from hydrogen peroxide. The oxygen-18 content was found slightly higher than the natural abundance value, and it came closer to the latter value when the reaction was carried out in the presence of anhydrous sodium sulphate. This fact suggests that it is probably the water formed in the course of the reaction that caused the production of oxygen containing oxygen-18 in excess of the natural abundance, presumably through the formation of free peroxybenzoic acid, which subsequently reacts with the peroxybenzoate anion to give oxygen.[4] Another possibility is a slight decomposition of sodium peroxybenzoate itself in methanol; separate experiments showed that sodium peroxybenzoate (^{18}O, 1·455%) decomposed completely in anhydrous methanol at 0° in 24 hr giving oxygen (^{18}O, 1·44%) in a 18% yield of the theoretical.

This mechanism of the evolution of oxygen from the peroxybenzoate anion and hydrogen peroxide will be valid also in aqueous solution and is formulated as follows:



Additional support for this mechanism, in which two H atoms are abstracted from a molecule of hydrogen peroxide, is afforded by the failure of alkyl hydroperoxides to react with sodium peroxybenzoate in methanol under otherwise the same conditions as with hydrogen peroxide. The results are shown in Table 3. No t-butyl hydroperoxide was consumed at all and only sodium peroxybenzoate was decomposed giving 14% of oxygen of almost the same oxygen-18 content as that in the original labelled peroxybenzoate. With ethyl hydroperoxide, the results were essentially the same as with t-butyl hydroperoxide, but the slightly lower oxygen-18 contents may be taken to indicate that some oxygen has come from the ethyl hydroperoxide.

Duke and Haas[5] have proposed the following tentative scheme for the decomposition of hydrogen peroxide in aqueous alkali on the basis of kinetic evidence:

This formulation seems to be reasonable in view of the now established mechanism of the reaction between the peroxybenzoate anion and hydrogen peroxide.

After the completion of the present work, McKeown and Waters[6] have shown that singlet oxygen is produced by decomposition of peroxy-acids in alkaline solution in the presence of hydrogen peroxide.

TABLE 1 ^{18}O CONTENT IN OXYGEN EVOLVED IN THE REACTION BETWEEN SODIUM PEROXYBENZOATE-(PEROXY-^{18}O) AND HYDROGEN PEROXIDE IN AQUEOUS SODIUM HYDROXIDE

$PhCO_3Na$ (^{18}O, 1·401%), H_2O_2 (^{18}O, 0·205%, natural abundance): under an argon atmosphere, at 0°C

NaOH N	$PhCO_3Na$ M	H_2O_2 M	^{18}O content (%) in O_2 Found	Calcd.[a]
10^{-2}	0·0284	0·0372	0·568, 0·589	0·723
	0·0235	0·0317	0·533	0·714
	0·0235	0·317	0·240, 0·234	0·287
10^{-3}	0·0288	0·0316	0·713, 0·670	0·775
	0·0245	0·0318	0·611	0·721
	0·0245	0·318	0·248, 0·243	0·282

[a] Calculated on the assumption that the exchange equilibration is complete before the evolution of oxygen.

TABLE 2. ^{18}O CONTENT IN OXYGEN EVOLVED IN THE REACTION BETWEEN SODIUM PEROXYBENZOATE-(PEROXY-^{18}O) AND HYDROGEN PEROXIDE IN ANHYDROUS METHANOL (4–6 ml)

$PhCO_3Na$ (^{18}O, 1·455%), H_2O_2 (^{18}O, 0·205%, natural abundance): under nitrogen atmosphere, at 0°C

$PhCO_3Na$ M	H_2O_2 M	Na_2SO_4	^{18}O%
0·0435	0·0480	none	0·236, 0·231
0·0435	0·0480	0·5 g	0·222
0·0363	0·480	none	0·245, 0·221
0·0363	0·480	0·5 g	0·204

TABLE 3. THE REACTION BETWEEN SODIUM PEROXYBENZOATE-(PEROXY-^{18}O) AND ALKYL HYDROPEROXIDES IN ANHYDROUS METHANOL (4–6 ML)

$PhCO_3Na$ (^{18}O, 1·455%), in the presence of anhydrous sodium sulphate (0·5 g), under nitrogen atmosphere, at 0°

ROOH M		$PhCO_3Na$ M	^{18}O%	Oxygen evolved, %[a]	Residual[b] peroxide, M
EtOOH	0·0480	0·0383	1·36	19	0·0540
			1·37	20	0·0533
	0·306	0·0348	1·25	39	0·298
			1·28	38	0·298
t-BuOOH	0·0321	0·0265	1·45	14	0·0336
			1·41	14	0·0339
	0·0955	0·0253	1·42	12	0·0936
			1·40	14	0·0937
none		0·0488	1·42	19	none
			1·45	16	none

[a] Yields were calculated on the assumption that one mole of oxygen is evolved from two moles of the peroxybenzoate decomposed

[b] Residual peroxide was estimated by the method of Wagner *et al.*[10]

EXPERIMENTAL

Materials. t-Butyl hydroperoxide was prepared from t-BuOH and H_2O_2 in the presence of H_2SO_4.[7] It was purified by precipitation as the Na salt from a soln in light petroleum by adding NaOH aq. The salt was filtered off and treated with dil H_2SO_4, and the resulting hydroperoxide was extracted with light petroleum. This procedure was repeated three times. Finally, the extract was dried over purified Na_2SO_4 and fractionally distilled to give the hydroperoxide, b.p. 39·0°–40·0° at 20 mmHg.

Ethyl hydroperoxide was prepared from diethyl sulphate and H_2O_2,[8] fraction boiling in a range of 90°–97° was dissolved in MeOH, and the soln dried over purified Na_2SO_4 and distilled. The distillate containing ethyl hydroperoxide and a little MeOH was treated with anhyd Na_2SO_4 and distilled again.

H_2O_2 (90%, stabilizer free) was dissolved in MeOH, and the soln dried over purified Na_2SO_4 before use.

Na_2SO_4 used for drying the materials was purified as follows: Na_2SO_4 (250 g) was dissolved in water (800 ml) and Cl_2 was bubbled through the soln at about 50° for 5 hr. It was then made alkaline with NaOH, boiled for about 10 min, filtered while hot, and cooled to precipitate $Na_2SO_4 \cdot 10H_2O$. The hydrate was recrystallized from de-ionized water three times and then dried at 80° to yield anhydrous sodium sulphate.

Acetone was refluxed with $KMNO_4$ for several hr and then distilled twice.

MeOH was distilled, dehydrated by refluxing with magnesium methoxide for several hr, and then distilled again.

Benzaldehyde was distilled and stored under an atmosphere of argon, and it was distilled immediately before use.

^{18}O was prepared by electrolyzing, with platinum electrodes, water enriched in ^{18}O (^{18}O content, 1·5%) in the presence of H_2SO_4 (20%).

Peroxybenzoic acid-(peroxy-^{18}O) was prepared by oxygenating benzaldehyde with ^{18}O:[9] Acetone (100 ml) and benzaldehyde (10 ml, 0·099 mol) were placed in a 3-necked, 200 ml, round-bottomed flask equipped with inlet tubes for ^{18}O and argon and an outlet tube for evacuation. The contents of the flask were solidified by chilling with liquid air, the flask was evacuated, the contents were thawed and the flask was filled with argon. The cycle of chilling, evacuation and thawing was repeated twice more to remove air, and finally the flask was filled with O_2 (^{18}O content, 1·57%). The soln was stirred vigorously with a magnetic stirrer under irradiation with UV light. The pressure of the O_2 was maintained at the atmospheric one throughout the reaction. After about 6 hr, when the rate of absorption of O_2 became very slow, the reaction was stopped. The yield of peroxybenzoic acid was 0·068 mole by iodometry. CH_2Cl_2 (80 ml) was added to the soln, benzoic acid was extracted with $NaHCO_3$aq (8·4 g in 200 ml water, used in 3 portions) and the organic layer was washed with water and dried over Na_2SO_4 (yield of peroxybenzoic acid, 0·055 mol). Peroxybenzoic acid-(peroxy-^{18}O) (3·0 g, 0·022 mol; purity 96–98%) was isolated from this soln by the usual procedure, and converted into the Na salt as described in the preceding paper.[1] The content of ^{18}O in the peroxide bond was determined by mass-spectrometry on the O_2 liberated, by means of ceric sulphate, from the H_2O_2 which is produced by hydrolysis of the labelled sodium peroxybenzoate in 1N NaOH.

Reactions of sodium peroxybenzoate-(peroxy-^{18}O) with hydrogen peroxide and alkyl hydroperoxides. The reactants were sealed in a tube equipped with a breakable seal as described[1] and left to stand at 0° for 24 hr, and the ^{18}O content of the O_2 formed was determined by using a mass-spectrometer (Model 21-103A, Consolidated Engineering Corporation).

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