# THE FORMATION OF PERACIDS BY THE PERHYDROLYSIS WITH ALKALINE HYDROGEN PEROXIDE\*

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Abstract—A high yield (ca. 90%) of perbenzoic acid has been obtained in the alkaline perhydrolysis of benzoyl peroxide by suppressing the decomposition of the peracid with excess alkali and a little magnesium sulfate in aqueous organic solvents. This perhydrolysis method has been applied to other substrates, e.g. benzoyl chloride, phthalic anhydride and acetyl chloride giving 85–90% yields. The perhydrolysis of benzoyl chloride has been shown to proceed, partially at least, through the intermediary formation of benzoyl peroxide.

MANY useful methods for the preparation of peracids have been reported in addition to those cited in Swern's review,<sup>1</sup> although the usual procedure is according to the equation:

$$RCO_2H + H_2O_2 \xrightarrow{H^2} RCO_3H + H_2O$$
(1)

Since this reaction is acid-catalysed and resembles the esterification of carboxylic acids,<sup>2,3</sup> several modifications are now available and more suitable for the syntheses of peracids as is the direct oxidation of aromatic and aliphatic peracids with 90–95%  $H_2O_2$  in methanesulphonic acid which is a good solvent as well as a strong acid or catalyst.<sup>4</sup>

Another method is the autoxidation of aldehydes, e.g. peracetic acid is obtained by the thermal decomposition of acetaldehyde monoperacetate produced by the low-temperature autoxidation of acetaldehyde,<sup>5</sup> and perbenzoic acid may be prepared by ozone-catalysed autoxidation of benzaldehyde.<sup>6</sup>

Alkaline alcoholysis of diacyl peroxide is another important method, but the yield is low, since one half of the acyl groups in the peroxide is lost as ester.<sup>7,8</sup>

- <sup>1</sup> D. Swern, Chem. Revs. 45, 1 (1949).
- <sup>2</sup> C. A. Bunton, *Peroxide Reaction Mechanisms* (edited by J. O. Edwards), p. 18. Interscience Publishers, New York (1961).
- <sup>3</sup> Y. Ogata and Y. Sawaki. Tetrahedron 21, 3381 (1965); Y. Sawaki and Y. Ogata, Bull. Chem. Soc. Japan 38, 2103 (1965).
- <sup>4</sup> L. S. Silbert, E. Siegel and D. Swern, J. Org. Chem. 27, 1336 (1962).
- <sup>5</sup> B. Phillips, P. S. Starcher and B. D. Ash, J. Org. Chem. 23, 1823 (1958).
- <sup>6</sup> C. R. Dick and R. F. Hanna, J. Org. Chem. 29, 1218 (1964).
- <sup>7</sup> G. Braun, Organic Syntheses Coll. Vol. 1; p. 431. Wiley, New York (1941).
- \* C. G. Overberger and R. W. Cummins, J. Am. Chem. Soc. 75, 4250 (1953).

<sup>\*</sup> Contribution No. 95.

$$\begin{array}{ccc} O & O & O \\ RCOOCR + R'O^{-} & \hline & RCOO^{-} + RCOOR' \end{array}$$

$$(2)$$

Moreover, this method requires rather troublesome steps via parent acid  $\rightarrow$  acyl chloride  $\rightarrow$  diacyl peroxide, and hence the reaction leads to low yields of peroxy acids. It is of interest to note that these shortcomings may be overcome by the alkaline perhydrolysis of acyl halides at low temperature (below  $-5^{\circ}$ ).<sup>9, 10</sup> Since magnesium sulfate is a good stabilizer for peroxides, the reaction may conveniently be carried out at room temperature in the presence of a little magnesium sulfate.<sup>11</sup>

We found that benzoyl peroxide (BPO) may easily be perhydrolysed to perbenzoic acid in alkaline aqueous organic solvents and that the decomposition of peroxides can be minimized by the use of excess alkali and a small amount of magnesium sulfate in a polyethylene flask. The perhydrolysis is also applied to some other hydrolysable carbonyl compounds, e.g. benzoyl chloride, acetyl chloride, benzoic anhydride and phthalic anhydride.

### Perhydrolysis of benzoyl peroxide (BPO)

BPO is easily perhydrolysed to perbenzoic acid in aqueous organic solvents according to the stoichiometric equation:

$$\begin{array}{cccc} O & O & O \\ RCOOCR + O_2H^- & \hline RCOO^- + RCOOH \end{array}$$
(3)

Since BPO is sparingly soluble both in water and in alcohol, the heterogeneous reaction mixture containing a suspension of powdered BPO was stirred magnetically at room temperature  $(20 \pm 2^{\circ})$ . The suspended BPO was converted to perbenzoic acid within 5 min in a good yield (*ca.* 90%). To minimize the decomposition of peroxides, *ca.* 0.04 mole of magnesium sulfate and *ca.* 3 moles of alkali for 1 mole of substrate was used in a polyethylene flask. The results are summarized in Table 1.

The rate of perhydrolysis of suspended BPO seems to depend on the solubility of BPO in the media. The perhydrolysis is almost complete within 5 min at  $20 \pm 2^{\circ}$  in a solvent of higher solubilizing power, e.g. 33% and 50% ethanol, 33% dioxan and 50% methanol, while the reaction is half-way even after 10 min and requires a longer reaction time in a solvent of lower solubility, e.g. 17% ethanol, 17% dioxan, 17% and 33% methanol.

It is well known that hydrogen peroxide is nearly  $10^4$  times as acidic as water and that  $O_2H^-$  is more reactive than  $OH^-$  by a factor of  $10^4$  for typical  $S_N2$ reactions,<sup>12</sup> while  $H_2O_2$  is only 35 times as nucleophilic as  $H_2O$  for  $S_N1$  reactions.<sup>13</sup> The present perhydrolysis of BPO should proceed by the  $S_N2$  mechanism, since perbenzoic acid was obtained in a high yield even with only a slight excess of  $H_2O_2$ (runs 7, 14 and 19) and its hydrolysis is very slow in the absence of  $H_2O_2$  (run 8). The stronger nucleophilicity of  $O_2H^-$  provides an explanation for the above results.

<sup>&</sup>lt;sup>9</sup> A. Kergomard and J. Bigou, Bull. Soc. Chim. Fr. 486 (1956); 334 (1958).

<sup>&</sup>lt;sup>10</sup> M. Vikas, Bull. Soc. Chim. Fr. 1501 (1959).

<sup>&</sup>lt;sup>11</sup> J. R. Moyer and N. C. Manley, J. Org. Chem. 29, 2099 (1964).

<sup>&</sup>lt;sup>12</sup> \* J. O. Edwards and R. G. Pearson, J. Am. Chem. Soc. 84, 16 (1962); <sup>b</sup> R. G. Pearson and D. N. Edginton, *Ibid.* 84, 4607 (1962).

<sup>13</sup> Ref. 2, p. 19.

The spontaneous decomposition of peroxides satisfies the second-order kinetics:<sup>14-16</sup>  $v = k[ROO^-][ROOH]$ . Therefore, the use of excess alkali, which results in the complete ionization of peracid, reduced the decomposition of the peracid. The decomposition of H<sub>2</sub>O<sub>2</sub> is known to be catalysed heterogeneously by the surface of glass vessels<sup>17</sup> and homogeneously by some metallic ions. EDTA is

No.	Solvent vol%	Reaction condition <sup>e</sup>	Recovered BPO	PhCO <sub>3</sub> H % yield <sup>®</sup>
1	33% EtOH		Trace	91-93
2	33% EtOH	(for 70 min)	0	90
3	33% FtOH	(at 30°)	Trace	91
4	33% EtOH	$[MgSO_{4}] \approx 0$	Trace	77
5	33% EtOH	in a glass flask	Trace	91
6	33% EtOH	0.5 g EDTA instead of MgSO <sub>4</sub>	Trace	78
7	33% EtOH	$0.075 \text{ mole } H_2O_2$	Trace	90
8	33% EtOH	$[H_2O_2] = 0$	44%	18(32)
9	33% EtOH	0-10 mole NaOH	17%	64(77)
10	17% EtOH		10%	77(85)
11	50% EtOH	_	Trace	90
12	17% Dioxan	_	14%	80(93)
13	33% Dioxan	-	0	93-94
14	33 % Dioxan	$0.075 \text{ mole } H_2O_2$	Trace	92
15	17% MeOH	_	80 %	17(85)
16	33% MeOH	<u> </u>	55%	38(85)
17	33% MeOH	(for 60 min)	Trace	81
18	50% MeOH	~	Trace	88- <b>90</b>
19	50% MeOH	0.075 mole $H_2O_2$	Trace	81
20	50 % McOH	$[MgSO_4] = 0$	Trace	72

TABLE 1. THE PREPARATION OF PERBENZOIC ACID BY THE REACTION OF BENZOYL PEROXIDE WITH ALKALINE HYDROGEN PEROXIDE FOR 10 MIN AT 20  $\pm$  2°

<sup>e</sup> Reaction conditions are as follows except when specially indicated. Initial amount of each reactant: NaOH = 6 g (0.15 mole), 30% H<sub>2</sub>O<sub>2</sub> = 15 ml (0.15 mole), MgSO<sub>4</sub> · 7H<sub>2</sub>O = 0.5 g (0.002 mole), (C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub> = 12.1 g (0.050 mole). BPO was finally added to the reaction mixture (150 ml) kept at 20 ± 2° in a polyethylene flask. <sup>b</sup> %Yield based on the stoichiometry that 1 mole of BPO yields 2 moles of perbenzoic acid (Eq. 3). Figures in parenthesis are % yield based on the consumed BPO.

generally used to suppress the homogeneous catalytic decomposition of peroxides by a trace of metallic ions; magnesium sulfate is also found to be effective.<sup>11</sup> In the present reaction, the addition of a little magnesium sulfate in a polyethylene flask effectively reduced the decomposition of peroxides (cf. runs 1 and 4, 19 and 20). Magnesium sulfate was found to be more useful than EDTA for the present preparation (run 6).

- <sup>14</sup> J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.* 58, 1846 (1962). And also see, K. Akiba and O. Simamura, *Chem. & Ind.* 705 (1964).
- <sup>15</sup> F. R. Duke and T. W. Haas, J. Phys. Chem. 65, 304 (1961).
- <sup>16</sup> E. Koubek, M. L. Haggett, C. J. Battaglis, K. M. Ibne-Rasa, H. Pyun and J. O. Edwards, J. Am. Chem. Soc. 85, 2263 (1963).
- <sup>17</sup> L. Erdey and I. Inczedy, Acta Chim. Acad, Sci. Hung. 7, 93 (1955).

## Perhydrolysis of benzoyl chloride

Moyer and Manley<sup>11</sup> used an equimolar mixture of sodium peroxide and benzoyl chloride together with a little sulfate to give perbenzoic acid in 75% yield in 54% ethanol and 60% yield in 54% methanol. According to their procedure the decomposition of peracid may occur because of the presence of equivalent amounts of acid and base at the end of the reaction. Further, benzoyl chloride should be attacked not only by  $O_2H^-$  but also by  $OH^-$  or  $OR^-$  competitively. Our experiments confirmed that the use of excess alkali and  $H_2O_2$  is effective for the reduction of alcoholysis and/or hydrolysis and the decomposition of peracid, resulting in a high yield (*ca.* 90%) of perbenzoic acid (Table 2), which supports the above assumption. Aqueous dioxan and ethanol are suitable solvents to give 92–93% yield and aqueous methanol may also be used but in slightly lower yield (88–89%). The decrease of the amount

Table 2. Perhydrolysis of Benzoyl chloride in the presence of magnesium sulfate. Temp.:  $20 \pm 5^{\circ}$  and time: 15 min. Initial amount of reactants in 100 ml solution: NaOH = 0.15 mole, MgSO<sub>4</sub> = 0.001 mole, H<sub>2</sub>O<sub>2</sub> = 0.15 mole, PhCOCI = 0.05° mole

No.	Solvent vol.%	Reaction condition <sup>a</sup>	Perbenzoic acid % yield
21	50% Dioxan		92:0*
22	30% Dioxan		93-0
23	30 % Dioxan	$0.075 \text{ mole } H_2O_2$	73-2
24	50% EtOH	_	92·1
25	50% MeOH	~-	8889
26	50% MeOH	$[MgSO_4] = 0$	73-0*
27	50% MeOH	MeOH was finally added	87·24
28	50 % MeOH	0.075 mole NaOH	7·5*
29	50% MeOH	0.075 mole H <sub>2</sub> O <sub>2</sub>	68·6
30	50% MeOH	Reaction time = $ca. 1 \min$	49·6 <sup>7</sup>

\* Reaction condition is as indicated in the title except specially noted.

<sup>b</sup> The formation of benzoyl peroxide was not observed only in this solvent.

<sup>c</sup> The decrease of total peroxide was ca. 15% in the absence of MgSO<sub>4</sub>.

<sup>4</sup> Methanol was finally added after completion of the formation of BPO.

\* 75% of total peroxide was decomposed.

<sup>f</sup> 27% of BPO was filtered off from the reaction mixture.

of excess  $H_2O_2$  resulted in a lower yield of peracid (runs 23 and 28). These features differ from the case of BPO where no decrease in yield was observed. This change in relative reactivity of nucleophiles with the change in the reactivity of the substrate is well known.<sup>18</sup> It is convincing that more reactive benzoyl chloride is more easily and less selectively attacked by nucleophiles than BPO.

The perhydrolysis of benzoyl chloride has been thought to give only perbenzoic acid, very little BPO being formed, in a mixed solvent capable of dissolving the chloride.<sup>10, 11</sup> It has been believed that among competing nucleophiles,  $O_2H^-$ ,  $OH^-$ 

and PhCO<sub>3</sub><sup>-</sup> for benzoyl chloride, only  $O_2H^-$  is active to form perbenzoic acid (reaction 4a).<sup>11</sup>

$$\int_{1}^{0} PhCCl + O_2H^- \longrightarrow PhCOOH + Cl^-$$
(4a)

$$\begin{array}{c} O & O & O \\ PhCCl + O_2H^- & \frac{OH^-}{-Cl^-} & PhCOO^- & \frac{PhCOCl}{-Cl^-} & PhCOOCPh \end{array}$$
(4b)

As the reaction proceeds, however, the concentration of  $PhCO_3^-$  rises, while that of  $O_2H^-$  drops, which would lead to the intermediary formation of a considerable amount of BPO (reaction 4b). The precipitation of BPO is actually observed. For example, *ca.* 27% of BPO was separated on filtration immediately after the addition of benzoyl chloride to the reaction mixture in 50% methanol (run 30). The intermediate BPO is then rapidly perhydrolysed under these conditions. No formation of BPO was observed in a solvent of 50% dioxan where the perhydrolysis of BPO is very fast. Therefore, both reaction pathways, 4a and (4b + 3), may be operative.

Table 3. The formation of peracids by the reaction of alkaline hydrogen peroxide with acid chlorides or anhydrides in 100 mL of 50 vol. % methanol at 20  $\pm$  5° for 15 min<sup>4</sup>

Bun no	Substants	Peracid, yield %	
Kull no.	Substrate	(Titrated)	(Extracted)
31	BPO	91.5	88·2
32	Benzoyl chloride	89-3	87.3
33	Benzoic anhydride	90-1	88.4
34	Phthalic anhydride	85-5	_
35°	Phthalic anhydride	89-0	82·7
36'	Acetyl chloride	70-6	
37	Maleic anhydride	87·5	<u> </u>

<sup>4</sup> Initial amount of reactants:  $MgSO_4 \cdot 7H_2O = 0.001$  mole, NaOH = 0.15 mole,  $H_2O_2 = 0.15$  mole and substrate = 0.050 mole. <sup>b</sup> Reaction in water with the reaction time of 5 min; monoper-

phthalic acid was extracted with ethyl ether.

\* Reaction time = 30 min.

#### **Application** to other substrates

The present perhydrolysis method may be applied to other substrates in 50% methanol and summarized in Table 3. Benzoic anhydride, phthalic anhydride, and maleic anhydride were perhydrolysed to give the corresponding peracids in 86-92% yield. A lower yield was obtained with acetyl chloride which is most reactive among these substrates.<sup>19</sup>

This method is also advantageous for the synthesis of monoperphthalic acid. An

<sup>&</sup>lt;sup>19</sup> The rate of hydrolysis of acetyl chloride is ca. 260 times as fast as that of benzoyl chloride, I. Ugi and F. Beck, Chem. Ber. 94, 1839 (1961).

improved method<sup>20</sup> for the Böhme procedure<sup>21</sup> must be carried out at low temperature below 0° with speedy treatment to minimize the decomposition of the peracid. The use of excess alkali and magnesium sulfate can stabilize the reaction mixture and hence the reaction can be carried out even at room temperature. The reaction employing grainy (ca. 5 mm in diameter) phthalic anhydride is possible and the reaction is complete within 5 min. The stirring of the reaction mixture for an additional 30 min resulted in only a slight decrease in the yield (ca. 82%).

No appreciable heat was evolved even by the rapid addition of BPO or benzoic anhydride, while a considerable evolution of heat was observed on the addition of the other substrates, and hence in this case the dropwise addition and external cooling with cold water were necessary.

#### EXPERIMENTAL

*Materials.* Benzoic anhydride was prepared from benzoic acid and acetic anhydride.<sup>22</sup> b.p. 183–186 (5 mm), m.p. 42–43° (lit.<sup>22</sup> 43°). The other organic materials were of chemically pure grade. NaOH, 30%  $H_2O_2$  and MgSO<sub>4</sub> · 7H<sub>2</sub>O were all of guaranteed grade. No significant difference in yield was observed on use of materials of extra pure grade.

Perhydrolysis of BPO. MgSO<sub>4</sub>  $\cdot$  7H<sub>2</sub>O (0.5 g, 0.002 mole), NaOH (6 g, 0.15 mole) and then 30% H<sub>2</sub>O<sub>2</sub> (15 ml, 0.15 mole) were dissolved in H<sub>2</sub>O (60 ml) in a polyethylene flask cooled to *ca*. 20° with cold water. MeOH (75 ml) was added and the soln maintained at 20°. Powdered BPO (12·1 g, 0.050 mole) was added in one portion to the mixture with magnetic stirring. After 10 min, the reaction mixture was poured into 20% H<sub>2</sub>SO<sub>4</sub> (*ca*. 150 ml) and the soln was extracted with 3 portions of 50 ml CHCl<sub>3</sub>. The titration of peracid indicated the presence of *ca*. 0.090 mole (90%) of perbenzoic acid. The results are listed in Table 1.

Perhydrolysis of benzoyl chloride, etc. A procedure similar to that for BPO was applied to other substrates, care being exercised in adding 0.050 mole of substrate with external cooling in ca. 3 min to avoid the violent reaction. In the case of the perhydrolysis of phthalic anhydride only water was used as a solvent. The results are listed in Tables 2 and 3.

Estimation of peracids. Peracids were titrated iodometrically in most cases. For the analysis of the mixture of  $H_2O_2$  and peracid,  $H_2O_2$  was rapidly titrated with 0.1N KMnO<sub>4</sub> in the cold, the remaining peracid being determined iodometrically.

In the case of monopermaleic acid, KMnO<sub>4</sub> aq. could not be used for the titration because of the reaction of KMnO<sub>4</sub> with the olefinic acid. Thus, monopermaleic acid was titrated by a novel procedure as follows: 2 ml of the acidifed reaction mixture was pipetted into *ca*. 5 ml of Me<sub>2</sub>SO (DMSO) in a 200 ml flask and the soln was allowed to stand for 5 min. *Ca*. 5 ml of 50% KI and 10 ml of 10% H<sub>2</sub>SO<sub>4</sub> together with 3 drops of 1% Na<sub>2</sub>MoO<sub>4</sub> were added, the liberated iodine being rapidly titrated with 0 1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>; this titre corresponded to the amount of H<sub>2</sub>O<sub>2</sub>. Total peroxide was determined iodometrically at the same time. The difference between the two titres corresponded to peracid, which was consumed by the oxidation of DMSO to dimethyl sulfone. H<sub>2</sub>O<sub>2</sub> were not consumed under these conditions. The results by this DMSO-KI method are consistent with those by KMnO<sub>4</sub>-KI method in the case of peracetic acid.

- <sup>20</sup> G. B. Payne, J. Org. Chem. 24, 1354 (1959).
- <sup>21</sup> H. Böhme, Organic Syntheses Coll. Vol. III; p. 619. Wiley, New York (1955).
- <sup>22</sup> H. T. Clarke and E. J. Pahrs, Organic Syntheses Coll. Vol. 1; p. 91. Wiley, New York (1941).

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