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Oxidation of Organic Compounds with Perborates or H_2O_2-Boric Acids[1)]

Yoshiro OGATA* and Hideo SHIMIZU

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

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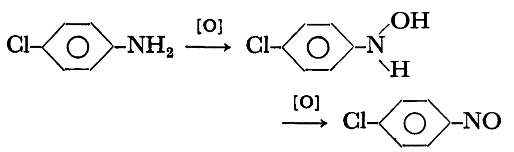
Synopsis. Perborate oxidation of *p*-chloroaniline to 4,4′-dichloroazobenzene and H_2O_2–boric acid hydroxylation of aromatics have been studied. The kinetic behavior suggests that the so-called sodium perborate is not peroxoborate but borate peroxyhydrate, H_2O_2 acquiring stronger electrophilicity by the coordination with boric acid which acts as Lewis acid rather than protic acid.

Perborates have received little attention as reagents for organic oxidations. Metha and Vakilwala reported that sodium perborate is a satisfactory reagent for the oxidation of anilines to azo compounds.[2)] However, no report seems to have appeared on the mechanism of perborate oxidation and the systems of H_2O_2–boric acids (boric acids: H_3BO_3, HBO_2, and B_2O_3). The present note deals with our attempt to elucidate the mechanism for the oxidation of *p*-chloroaniline with perborates and hydroxylation of aromatics with H_2O_2–boric acids reagents.

Results and Discussion

Oxidation of p-*Chloroaniline.* *p*-Chloroaniline was oxidized by sodium or ammonium perborates in acetic acid to give 4,4′-dichloroazobenzene. Azobenzene is obtained as a condensation product of unreacted aniline with nitrosobenzene formed *via* phenylhydroxyamine[3,4)] (Eqs. 1 and 2).



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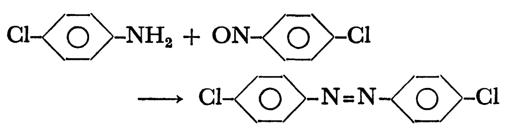


(2)

Oxidation can also be achieved by H_2O_2–AcOH. The rates of disappearance of perborates or H_2O_2 (0.02—0.04 M) were measured iodometrically in 100 or 75% aq AcOH at 50 °C, where *p*-chloroaniline is in large excess (0.5 M) (Table 1). The rates are pseudo-first order in perborates or H_2O_2: $v=k_{\text{obsd}}[\text{perborates or } H_2O_2]$. There is no possibility that the actual oxidizing agent is peracetic acid,[5)] since the rate for peracetic acid formation (Table 2) is smaller than that of aniline oxidation. Azobenzene should be produced mainly by direct oxidation of aniline with another oxidizing species.

Table 1. Rates for oxidation of *p*-chloroaniline by perborates, H_2O_2, H_2O_2–H_3BO_3, or AcOOH in acetic acid at 50 °C[a)]

Oxidizing agent	$k_{\text{obsd}}\times 10^5\ (s^{-1})$[b)] In 100% AcOH	In 75% aq AcOH
$NaBO_3$	66.0	5.33
NH_4BO_3	45.8	4.88
H_2O_2	9.8	4.06
H_2O_2–H_3BO_3[c)]	—	4.41
AcOOH	too fast to measure	too fast to measure

a) [*p*-chloroaniline]=0.5 M, [oxidizing agent]=0.02—0.04 M. The yields of 4,4′-dichloroazobenzene were *ca.* 30% in each case under these conditions. b) The pseudo-first order rate constant with respect to oxidizing agent. c) H_2O_2: H_3BO_3=1: 1. H_3BO_3 is insoluble in 100% AcOH.

Table 2. Rates for the formation of peracetic acid by several peroxide systems in acetic acid at 50 °C

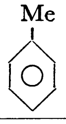
Oxidizing agent	$k_{\text{obsd}}\times 10^5\ (s^{-1})$[a)] In 100% AcOH	In 75% aq AcOH
$NaBO_3$	9.66	1.39
NH_4BO_3	3.30	1.17
H_2O_2	1.75	1.05
H_2O_2–H_3BO_3[b)]	—	1.25

a) The pseudo-first order rate constant with respect to the oxidizing agent. b) H_2O_2: H_3BO_3= 1: 1. H_3BO_3 is insoluble in 100% AcOH.

In 100% AcOH, apparent first-order rate constants (k_{obsd}) for sodium and ammonium perborates are respectively 6.7 and 4.7 times greater than those for H_2O_2, but in 75% aq AcOH the rate constants become comparable to those with H_2O_2. This can be explained as follows: the so-called perborate is not peroxoborate but borate peroxyhydrate.[6)] Thus, in excess water, H_2O_2 is readily separated from borate, the oxidation being performed by liberated H_2O_2, where the rate is analogous to that by H_2O_2 alone. In 100% AcOH, H_2O_2 remains coordinated with boric acid which is formed from metal borate in AcOH, the electrophilicity of H_2O_2 thus increasing. When an equivalent amount of boric acid is added to H_2O_2–75% aq AcOH system, the rate increases slightly (Table 1). The protonation of H_2O_2 by boric acid is negligible in AcOH, since acetic acid is a much stronger acid than boric acid.[7)] In conclusion, boric acid should coordinate with H_2O_2 as Lewis acid but not protic acid to increase the electrophilicity of H_2O_2.

Hydroxylation of Aromatics. It has been reported that aromatic hydroxylation occurs by H_2O_2 in the presence of Lewis acid such as BF_3[8a)] or $AlCl_3$,[8b)] where the hydroxylation might take place by HO^+ formed from H_2O_2 by the coordination of Lewis acid. Aromatic compounds were hydroxylated also with H_2O_2 in ether in the presence of H_3BO_3, HBO_2, or B_2O_3 (heterogene-

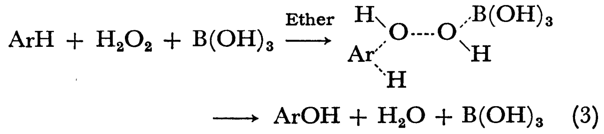
Table 3. Hydroxylation of anisole and toluene by H_2O_2–boric acids in ether at 100 °C for 1 h

Substrate[a]	Yield of monohydroxylated products (%)		
	H_3BO_3	HBO_2	B_2O_3
	54.6 (56:44)[b]	35.7 (51:49)[b]	84.5 (55:45)[b]
	6.7 (73:27)[c]	4.8 (67:33)[c]	45.1 (66:34)[c]

a) Substrate is in large excess. b) Ortho *vs.* para ratio. *m*-Isomer was not detected. c) Ortho *vs.* para-meta ratio. *m*- and *p*-isomers could not be separated. *m*-Isomer would not be produced because of the electrophilic nature of the reagent.

ous) at 100 °C (Table 3),[9] no reaction taking place by H_2O_2 alone under similar conditions.

Boric acids act as Lewis acid, but not protic acid in H_2O_2–boric acids, since the yield is the highest in the case of B_2O_3, which has no proton but is considered to the strongest Lewis acid among the three. For example with H_3BO_3:



On the other hand, sodium and ammonium perborates are basic and unable to form HO^+ from H_2O_2, although they can give free boric acid in acetic acid.

Experimental

Materials. The chemicals except ammonium perborate are commercial products of first grade. Ammonium perborate was prepared from ammonium borate and H_2O_2 by Tsal's method.[10] Guaranteed boric anhydride free of water was used.

Oxidation of p-*Chloroaniline.* The reactions of large excess *p*-chloroaniline (0.5 M) with sodium and ammonium perborates or H_2O_2 (0.02—0.04 M) were carried out in 100% and 75% aq AcOH at 50 °C. The reaction with H_2O_2 by addition of an equivalent amount of H_3BO_3 was carried out in 75% aq AcOH. The products were identified by GLC analysis in comparison with the corresponding authentic specimen. The rates were followed by determining the disappearance of the oxidizing agent by iodometry.

Rate for Formation of Peracetic Acid. The rates for peracetic acid formation from oxidizing agents (0.02—0.04 M) and AcOH were followed by determining the disappearance of the oxidizing agents by titration with $KMnO_4$.[11] The oxidizing agents were oxidized by $KMnO_4$, but peracetic acid formed was not oxidized.

Hydroxylation of Aromatics. A large excess of anisole (370 mmol) or toluene (435 mmol) was mixed with H_2O_2 (6 mmol) in Et_2O (10 ml). The solvent ether was removed in a vacuum until a pressure of 40 mmHg was attained. The reaction mixture was stirred vigorously with H_3BO_3, HBO_2, or B_2O_3 (15 mmol) at 100 °C for 1 h. The products were identified by GLC analysis with the authentic specimen.

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