Tetrahedron Letters,Vol.24,No.44,pp 4847-4850,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

Fe(III)-CATALYZED HYDROXYLATION OF BENZENE WITH H_2O_2 IN THE PRESENCE OF QUINONES

Seizo Tamagaki, Kenji Suzuki, Hiromu Okamoto, and Waichiro Tagaki*
Department of Applied Chemistry, Faculty of Engineering,
Osaka City University, Sugimoto 3-chome, Sumiyoshi-ku,
Osaka 558, Japan

In the presence of quinones as cocatalysts, Fe^{3+}-catalyzed hydroxylation of benzene with H_2O_2 provided phenol in moderate yields. 1,2-Naphthoquinone-4-sulfonate facilitated the hydroxylation with much greater efficiency.

Recently, attention has been focused on the direct formation of phenols from the corresponding aromatic compounds.[1] In particular, the hydroxylation with H_2O_2 in the presence of metal catalyst, for example, Fe^{2+}-H_2O_2 (Fenton's reagent) is of potentially practical importance and its mechanism has been the subjects of extensive studies.[2] However, the Fenton reaction itself requires large amounts of Fe^{2+}, which seriously limits the possibility of synthetic utility of this and closely related reactions.[3]

On the other hand, little attention has been paid to the hydroxylation using the combination of Fe^{3+} with H_2O_2 due to the slow rate of reaction and the low yield of phenol.[4] In this paper, we would like to show that the hydroxylation of benzene with Fe^{3+}-H_2O_2 can be made catalytic in Fe^{3+} by using a quinone as the cocatalyst.

A typical reaction was carried out under a nitrogen atmosphere at ambient temperature in a two-phase system of H_2O (50 mL) and benzene (2 mL) containing $Fe_2(SO_4)_3$ (0.05 mmol) and a quinone (0.1 mmol). H_2O_2 (1 mmol) was added to the solution all at once and the mixture was mechanically shaken during the course of the reaction. The standard procedure to determine the phenol yield was similar to those described previously.[5] The phenol yields were all based on H_2O_2 added.

Table shows the results of the hydroxylation in the presence of various quinones and other electron-transfer reagents, for comparison. In any case, phenol was obtained as the major product. No appreciable amount of byproducts

Table. Hydroxylation of benzene with Fe^{3+}-H_2O_2 in the presence of quinones[a)]

Cocatalyst	mmol	Fe^{3+}, mmol	Phenol Yield, %
none	0.1	0.1	1.9
p-benzoquinone	0.1	0.1	30.7
	0.01	0.01[c)]	b)
2,5-dimethyl-p-benzoquinone	0.1	0.1	32.1
1,2-naphthoquinone	0.1	0.1	30.1
anthraquinone-2-sulfonate	0.1	0.1	32.0
anthraquinone-2,7-disulfonate	0.1	0.1	32.6
anthraquinone-2,6-disulfonate	0.1	0.1[d)]	1.5
	0.1	0.1	36.1
	0.1	0.1[e)]	38.1
	0.1	0.1[f)]	1.5
	0.01	0.01[c)]	0.2
anthraquinone-1,5-disulfonate	0.1	0.1	3.7
anthraquinone-1,8-disulfonate	0.1	0.1	3.6
1,2-naphthoquinone-4-sulfonate	0.1	0.1	39.0
	0.1	0	0
	0.01	0.1	41.4
	0.01	0.01[c)]	33.1
	0.01	0.002[c)]	17.1
	0.01	0.002[g)]	22.6
Cu^{2+}	0.1	0.1	19.1
phenazine methosulfate[1a)]	0.1	0.1	22.5

a) Unless otherwise noted, the conditions were the same as described in the text; shaken for 2.5 h. The solutions were not buffered to show initially pH 3.0. For c) and d), the pHs of the reaction media were adjusted with H_2SO_4 to 3.0 and 1.7, respectively, and for e), f), and g), with NaOH to 3.5, 5.5, and 4.4, respectively.

b) Detected, but a trace amount.

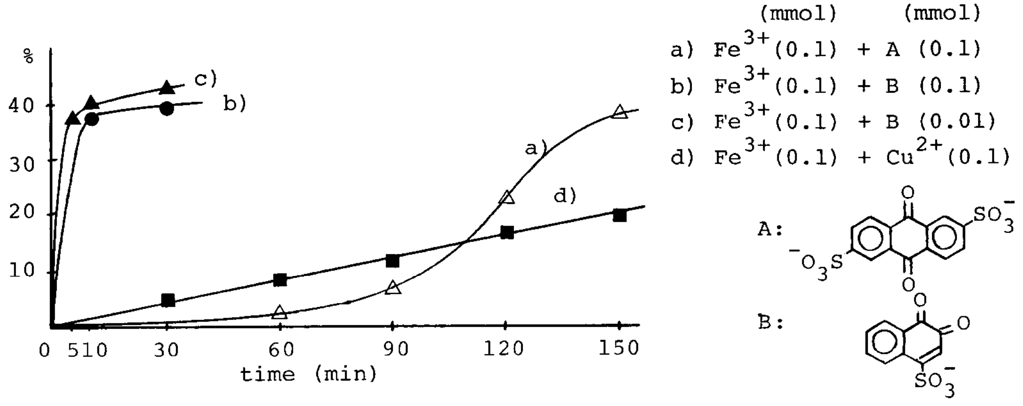

Figure. The time course of the hydroxylation. Phenol yield against time.

were found except for only traces of biphenyl and hydroquinone. In general, the yields of phenol were constantly greater than 30 %.6) However, anthraquinone-1,5 or 1,8-disulfonate exhibited no activity. This failure of these disulfonates to accelerate the reaction may be due either to decreasing oxidizing power of the quinones7) or to increased steric hindrance to approach of, presumably, the hydroxycyclohexadienyl radical by two sulfonate groups located at the peri-positions of the quinone-carbonyl groups.8) 3,5-Di-t-butyl-o-benzoquinone, 2,3,5,6-tetramethyl-p-benzoquinone, and 1,4-naphthoquinone (not shown in Table) were also inefficient which seems to be attributed to their high insolubility in the aqueous phase rather than any other factors.

The reaction was pH dependent. Namely, the phenol yields for anthraquinone-2,6-disulfonate or 1,2-naphthoquinone-4-sulfonate, for example, were only slightly different in weakly acidic media ($3.0 \lesssim pH \lesssim 4.5$), but went remarkably down to less than 1.5 % when the pH of the medium was decreased to 1.7 or increased to 5.5. The reduction of yield is not a result of the formation of biphenyl or any other byproducts at the expense of phenol, but due to no appreciable consumption of H_2O_2.

A typical time dependence of the phenol yield is indicated in the Figure, in which the catalytic activity of two typical water-soluble quinones, 1,2-naphthoquinone-4-sulfonate and anthraquinone-2,6-disulfonate, are compared; with the latter sulfonate, the reaction was initially slow, accompanied with a definite induction period, to finally give rise to 36.1 % of phenol.8,9) Cu^{2+} was also equally effective and provided phenol in a slightly reduced yield. On the other hand, when the former sulfonate was used, even if in small quantities, a rapid reaction took place, affording phenol in ca. 40 % yields within 5 min. Apparently, this quinone cocatalyst promotes the hydroxylation with a rate at least 30 times higher than that in the presence of the disulfonate, and the turnover of Fe^{3+} reaches greater than 100.

In conclusion, certain quinones play a vital role in the Fe^{3+}-promoted hydroxylation of benzene with H_2O_2, generally giving moderate yields of phenol. 1,2-Naphthoquinone-4-sulfonate is remarkably effective as the cocatalyst.10) Thus, the high activity of the present catalyst system, leading to a cleaner reaction with no dark deposit, has almost certainly much synthetic utility.

Further study on the mechanism and scope of this hydroxylation is currently in progress. The details will be reported elsewhere in the near future.

References

1) a) H.W. Richter and W.H. Waddell, J. Am. Chem. Soc., 104, 1666, 4630 (1982); b) D.M. Jerina, CHEMTECH., 1973, 120; c) A.I. Cederbaum, E. Dicher, and G. Cohen, Biochem., 19, 3698 (1980); d) B.B. Brodie, J. Axelrod, D.A. Shore, and S. Udenfriend, J. Biol. Chem., 208, 741 (1954); e) D.A. Hamilton, J.P. Freidman, and P.M. Campbell, J. Am. Chem. Soc., 88, 5266 (1966); f) V. Ullich,

D. Hay, J. Staudinger, H. Buech, and W. Rummelm, Biochem. Pharmacol., 16, 2237 (1967); g) M.E. Kurz and G.J Johnson, J. Org. Chem., 36, 3184 (1971); h) H. Hart, Acc. Chem. Res., 1971, 337; i) M. Fujihara, Y. Satoh, and T. Osa, Chem. Lett., 1981, 1053.

2) H.J.H. Fenton, J. Chem. Soc., 65, 899 (1894); C. Walling, Acc. Chem. Res., 8, 125 (1975).

3) J.R.L. Smith and R.O.C. Norman, J. Chem. Soc., 1963, 2897; C. Walling and D.M. Camaioni, J. Am. Chem. Soc., 97, 1604 (1975).

4) W.G. Barb, J.H. Baxendale, P. George, and K.R. Hargrave, Trans. Faraday Soc., 47, 591 (1951); M.A. Brook, L. Castle, J.R. Linsay Smith, P.R. Sleath, R. Higgins, and K. Moris, J. Chem. Soc., Perkin Trans., II, 1982, 687.

5) K. Hotta, S. Tamagaki, Y. Suzuki, and W. Tagaki, Chem. Lett., 1981, 789.

6) In such cases, no appreciable amounts of remaining H_2O_2 could be detected when tested with potassium iodide starch paper.

7) K.B. Patel and R.L. Wilson, J. Chem. Soc., Faraday Trans., I, 69, 814 (1973).

8) Various quinones were reported to oxidize hydroxycyclohexadienyl radicals to the corresponding phenols: N.V. Raghavan and S. Steeken, J. Am. Chem. Soc., 102, 3495 (1980). The same reaction appears to be involved during the course of the present hydroxylation.

9) Preliminary results suggest that the rates of electron transfer between the pairs of Fe^{3+}/Fe^{2+} and quinone/hydroquinone is important in the present system as in a non-classical Fenton system (see ref. 1a).

10) Under the standard conditions (0.1 mmol Fe^{3+}, 0.1 mmol 1,2-naphthoquinone-4-sulfonate, and 1 mmol H_2O_2), anisole and phenylacetic acid (1 mmol each) gave methoxyphenols (11.2 %yield; o:m:p=76.5:2.7:20.8 %) and hydroxyphenylacetic acids (30.4 % yield; o:m:p=48:26:26 %), respectively.

(Received in Japan 18 July 1983)