Tetrahedron, Vol. 37, pp. 1485 to 1486, 1981
Printed in Great Britain.

0040-4020/81/081485-02$02.00/0

AROMATIC HYDROXYLATION WITH PEROXYMONOPHOSPHORIC ACID[1]

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(*Received in Japan* 28 *July* 1980)

Abstract—Aromatic hydroxylation of mesitylene, phenol and anisole (ArH) with peroxymonosphosphoric acid (H_3PO_5) in acetonitrile has been studied. H_3PO_5 is shown to be an effective reagent for aromatic hydroxylation, the reactivity being comparable to that with CF_3CO_3H. Mesitylene gives mesitol (over 70%). The hydroxylation with H_3PO_5 is *ca* 100 fold faster than that with $MeCO_3H$ or $PhCO_3H$. The rate equation is: $v = k_2[ArH][H_3PO_5]$ instead of our previous one. The oxidation is catalyzed by H_2SO_4, giving a linear plot of log k_2 vs H_0 with a slope of 1.26 for phenol and 1.17 for mesitylene.

Since the first preparation of H_3PO_5 in 1910,[2] its preparation,[3,4] decomposition,[5] dissociation constants,[6] and a few reports[7] on its reaction appeared. Recently, we reported on the H_3PO_5 oxidations of acetophenones,[8] tertiary amines,[9] *trans*-stilbene,[10] tetrahydrofuran,[11] and phenols.[12]

Although aromatic hydroxylation with various peroxy reagents have been studied,[13-18] there are few kinetic studies because of the further oxidation of hydroxy aromatics formed. Some preparative and kinetic data by minimizing the further oxidation is the subject of this paper.

RESULTS AND DISCUSSION

Mesitylene. In general, aromatic hydroxylation gives products which are more easily oxidized than the original aromatics but in the case of mesitylene, all *o*- and *p*-positions to OH in the produced mesitol are methylated; hence further oxidation is very slow, and thus good yield of monohydroxylation is possible.

Addition of H_3PO_5 to mesitylene in acetonitrile led to an exothermic reaction, the solution turned to brown. Thus mesitylene gave mesitol together with a small amount of byproduct, 2,3,5-trimethylbenzoquinone.[17] With excess mesitylene, a relatively good yield (74%) of mesitol was obtained by the suppression of further oxidation. When the amount of mesitylene was duplicated, the yield fell to 31%. These yields are based on H_3PO_5 used, so that 31% yield becomes 77% based on the consumed mesitylene. It was reported that the yield of mesitol from excess mesitylene was 88% with CF_3CO_3H–BF_3 and 45% with CF_3CO_3H alone,[19] and that mesitylene with equimolar CF_3CO_3H gave mesitol (66%) along with trimethylbenzoquinone (13%)[17] based on consumed mesitylene. Hence H_3PO_5 hydroxylation is comparable to CF_3CO_3H hydroxylation.

Mesitylene is a convenient substrates for kinetic study because of little further oxidation especially with excess substrate. The kinetic data in acetonitrile as solvent are shown in Table 1. The rate was followed by iodometry of H_3PO_5. The rate is expressed as:

$$v = k_2[\text{mesitylene}][H_3PO_5].$$

The equation is different from our previous report on phenol.[12] Hence we reinvestigated hydroxylation of phenol.

Phenol and anisole. Excess phenol or anisole was used, H_3PO_5 being followed iodometrically; the kinetic is expressed as follows and listed in Table 1.

$$v = k_2[ArH][H_3PO_5].$$

Hence, the values of $k_2 \times 10^5\ M^{-1}\ s^{-1}$ are 19.3 (25°) and 36.7 (30°) for phenol, 8.51 (30°) for anisole and 46.9 (30°) for mesitylene (Table 1).

The more complex rate equation reported by us, which led to a complex mechanism, may be wrong, owing to the use of excess H_3PO_5, giving rise to abnormal acid catalysis.

Effect of acidity. A plot of log k_2 vs H_0 (acidity function) for the H_2SO_4-catalysed reactions of phenol and

Table 1. Second-order rate constants for H_3PO_5 hydroxylation of aromatic compounds

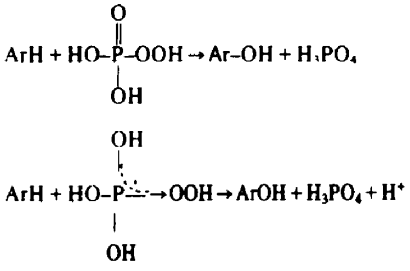
temp °C	ArH	$[ArH]_o$[a] M	$[H_3PO_5]_o$ M	$k_2 \times 10^4$ $M^{-1}\ s^{-1}$
25.0	Phenol	0.100	0.010	2.08
		0.200	0.010	1.99
		0.300	0.010	1.85
		0.500	0.010	1.80
		0.200	0.005	1.90
		0.200	0.010	1.99
		0.200	0.015	1.91
		0.200	0.020	1.97
30.0	Phenol	0.200	0.005	3.81
		0.200	0.010	3.58
		0.200	0.015	3.63
		0.200	0.020	3.67
30.0	Anisole	0.100	0.010	0.842
		0.200	0.010	0.833
		0.500	0.010	0.786
		0.200	0.005	0.833
		0.200	0.010	0.833
		0.200	0.015	0.833
		0.200	0.020	1.000
30.0	Mesitylene	0.100	0.010	4.90
		0.200	0.010	4.80
		0.500	0.010	3.95
		0.200	0.005	4.72
		0.200	0.010	4.80
		0.200	0.015	4.81
		0.200	0.020	4.83

[a] $[\ ]_o$ means initial concentration

mesitylene gave straight lines with a slope of 1.26 for phenol and 1.17 for mesitylene (Fig. 1), suggesting a proton participation at the transition state. In other words, the rate for acid-catalyzed oxidation of phenol is expressed as follows at 25°, where $-\log h_0 = H_0$.

$$v = 1.70 \times 10^{-4} h_0^{1.26} [\mathrm{PhOH}][\mathrm{H_3PO_5}].$$

Mechanism. The observed rate equation and acidity effect suggest a mechanism involving simultaneous attacks of unprotonated and protonated H_3PO_5 on aromatics.



Comparison with peroxycarboxylic acid. The reactivity of H_3PO_5 was compared with percarboxylic acid in the same solvent acetonitrile and listed in Table 2.

The rate with H_3PO_5 is *ca* 100 fold faster than that with peracetic acid, so that H_3PO_5 is a much more effective oxidant than peracetic and perbenzoic acids and comparable to perfluoroacetic acid in view of the yields reported in the literature.[17,19]

EXPERIMENTAL

Materials. Acetonitrile was distilled from H_2SO_4, then from P_2O_5 through a glass-joint packed column and fractionated, b.p. 81–82°. The careful purification is essential, since ordinary acetonitrile may be contaminated with water, unsaturated nitriles and amines, etc. which disturb kinetic study. Phenol, anisol, and mesitylene were of guaranteed grade and used without further purification. H_3PO_5 was prepared from P_2O_5 and 90% H_2O_2.[8]

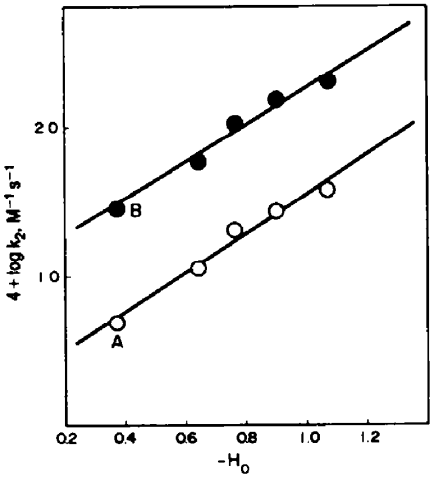


Fig. 1. Effect of acidity on the second-order rate constant k_2 in MeCN for PhOH at 25° (A) and mesitylene at 30° (B).

Table 2. Comparison of rates of H_3PO_5 with those of CH_3CO_3H for some aromatics

Substrate	k_2 $10^3(M^{-1}s^{-1})$[a]		$k_{H_3PO_5}/k_{CH_3CO_3H}$
	H_3PO_5	CH_3CO_3H	
Mesitylene	19.1	0.050	390
Phenol	6.9	0.048	140
Anisole	4.0	0.039	110

[a] Second-order rate constant at 30° in CH_3CN–H_2SO_4 (H_0=-1.07)

Products. Glc analysis was done with a Yanagimoto G 180 gas chromotograph using a column of Silicone OV-17 on Shimalite W. Products were identified by means of glc, NMR and IR, and estimated by glc using biphenyl as an internal standard.

Kinetics. For the rate measurements, H_3PO_5 was determined iodometrically in 10% aqAcOH, and the rate constants were calculated on the basis of dublicate or triplicate experiments. The spontaneous decomposition of H_3PO_5 without substrate in purified acetonitrile was negligibly slow.

Oxidation of mesitylene. A soln of H_3PO_5 (0.5 mmol) in acetonitrile was added ot a soln of mesitylene (10 mmol) in acetonitrile (10 ml), and the mixture was kept at 25° for 4 hr. Then the soln was extracted with ether, dried and analysed by glc, giving mesitol (0.37 mmol, 74%).

A soln of H_3PO_5 (3.5 mmol) in acetonitrile (3 ml) was added to a soln of mesitylene (7.2 mmol) in acetonitrile (7 ml), and kept at 25° for 4 hr, giving mesitol (1.08 mmol, 31% based on H_3PO_5 and 77% based on mesitylene consumed) along with 2,3,5-trimethylbenzoquinone.

Acidity function. Acidity function of an acetonitrile-H_2SO_4 soln was measured by the ordinary spectrophotometry using *p*-nitroanaline as an indicator. Concentration (N) of H_2SO_4 and acidity function (H_0) were: 0.020, −0.37; 0.051, −0.64; 0.103, −0.76; 0.154, −0.90; 0.206, −1.07.

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