

OXIDATION OF SUBSTITUTED TOLUENES BY OXYGEN IN THE PRESENCE OF  
Fe OR Cu POWDER

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The recently discovered reaction in which saturated hydrocarbons are oxidized by molecular oxygen in the presence of a soluble iron-containing complex, metallic zinc, pyridine, and acetic acid (the Gif<sup>IV</sup> system) has the following distinguishing features in comparison with other oxidation processes involving oxygen: Attack largely occurs at the secondary carbon atom and the main products are ketones [1, 2]. The same features have also been noted for the coupled-oxidation reaction of an alkane and Fe or Cu powder in pyridine in the presence of CF<sub>3</sub>COOH and H<sub>2</sub>O [2-4]. Two alternative mechanisms have been proposed for this process. According to the first hypothesis [1], in the presence of a reducing agent Fe(II) and O<sub>2</sub> form an Fe-O oxenoid species [2, 4] that inserts itself into a C-H bond, resulting in the formation of a carbene complex among other organometallic compounds [5]. According to the second hypothesis [3, 6], an HO<sub>2</sub> radical interacts with protonated pyridine PyH<sup>+</sup> to form the solvated oxygen cation PyO<sup>+</sup>.

In this work we investigated oxidation of various substituted toluenes by a system similar to that described, with the aim of gaining additional information on the character of the reaction from determination of the effect of substituents in the toluene ring on the rate of oxidation. We found that mixing a solution of toluene or a derivative in aqueous acetone or pyridine in the presence of Fe or Cu powder and CF<sub>3</sub>COOH in air leads to oxidation of the substrate with formation of the corresponding phenols and substituted benzaldehydes (oxidation does not occur in the presence of Zn powder). We note that the reactions proceeded only to a slight extent (oxidation ceased when there was still a large excess of the original substrate and metal over products). According to PMR data, slight amounts of benzyl alcohols and benzoic acids are formed in these conditions. In the reaction with toluene itself, the ratio of rates of attack of one C-H bond in the ring (the average of three positions) and in the methyl group falls on changing the solvent from acetone (8 and 6.5 for Cu and Fe, respectively) to pyridine (1 and 4.5, respectively). Thus, using pyridine the rates of attack on a bond of the aromatic ring are somewhat higher than in acetone. We note that our measured cresol/benzaldehyde ratio (per C-H bond capable of participating in the oxidation reaction) in the oxidation of toluene by the FeSO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system in water is equal to 8.

The method of competing reactions was used to measure relative rates of formation of substituted benzaldehydes in oxidation of the corresponding toluene derivatives. The results obtained are shown in Table 1. It is evident that, for both Fe and Cu and for the two solvents, the reaction rate is weakly dependent on the nature of the substituent in the toluene ring. In most cases introduction of a substituent (electron-donor or electron-acceptor) into the aromatic ring increases the rate. We note that a weak dependence of reaction rate on ring substituent is characteristic of processes in which a hydrogen atom is abstracted from the methyl group of toluene by free radicals [7-9]. Thus, the relative rates of hydrogen-atom abstraction from the methyl group of p-XC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> compounds by the C<sub>6</sub>H<sub>5</sub>· radical at 60°C varies in the following order of X [10]: C<sub>6</sub>H<sub>5</sub>O (0.97), CH<sub>3</sub> (1.47), H (1.00), Cl (1.07), NO<sub>2</sub> (0.81).

In addition, the method of competing reactions was used to determine relative rates of oxidation of benzyl alcohol (to benzaldehyde) and ethylbenzene (to acetophenone) by the system Fe powder-CF<sub>3</sub>COOH-H<sub>2</sub>O. When acetone is used as the solvent C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH is oxidized 8.7 times faster than C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>5</sub>, whereas in pyridine this ratio falls to 1.3. These data are in agreement with previously published results [3]. The rate of attack on the bond of the CH<sub>2</sub> group in ethylbenzene relative to the same for the CH<sub>3</sub> group in toluene during oxidation by oxygen in the presence of Fe powder falls somewhat when the solvent is changed from acetone (5.9) to pyridine (3.9).

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TABLE 1. Relative Rates of Oxidation of the Methyl Group in Substituted Toluenes by Diatomic Oxygen in the Presence of Metal Powders and  $\text{CF}_3\text{COOH}$  (calculated per substrate C-H bond)

Substrate	Fe		Cu	
	in acetone	in pyridine	in acetone	in pyridine
$\text{C}_6\text{H}_5\text{CH}_3$	1.0	1.0	1.0	1.0
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$	1.5	1.8	1.5	2.0
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	1.0	1.5	0.9	3.0
$m\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$				1.4
$m\text{-ClC}_6\text{H}_4\text{CH}_3$	1.3	1.5	1.0	1.3

#### EXPERIMENTAL

A Bruker SXP-4-100 apparatus (90 MHz,  $\text{CDCl}_3$  solvent) was used to measure  $^1\text{H}$  NMR spectra. To determine relative rates of oxidation, a solution of two toluene derivatives (5 mmole of each) and 0.5 ml  $\text{H}_2\text{O}$ , 0.5 ml  $\text{CF}_3\text{COOH}$ , and 5 ml acetone or 3 ml pyridine were stirred vigorously in air with Fe or Cu powder (0.5 g) for 1 h. Then an aqueous HCl solution was added, followed by extraction with chloroform. The combined extract was washed with water,  $\text{NaHCO}_3$  solution, and water, then dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residue partitioned on silica-gel plates (1:5 acetone-hexane eluant). Bands corresponding to substituted benzaldehydes were isolated and ratio determined in the mixture by integration of the CHO-group singlets in the PMR spectra. The following pairs of  $\text{XC}_6\text{H}_4\text{CH}_3$  substrates were used, where X is:  $p\text{-CH}_3\text{-H}$ ,  $m\text{-Cl-H}$ ,  $p\text{-OCH}_3\text{-H}$  (reaction with Cu in acetone);  $p\text{-CH}_3\text{-H}$ ,  $m\text{-Cl-H}$ ,  $p\text{-OCH}_3\text{-H}$  (Fe in acetone);  $p\text{-CH}_3\text{-H}$ ,  $m\text{-Cl-H}$ ,  $p\text{-OCH}_3\text{-H}$ ,  $p\text{-CH}_3\text{-H}$ ,  $m\text{-CH}_3\text{-H}$  (Cu in pyridine);  $p\text{-CH}_3\text{-H}$ ,  $o\text{-OCH}_3\text{-H}$ ,  $m\text{-Cl-H}$  (Fe in pyridine).

Other reactions and analysis of the products were conducted in a similar fashion.

#### CONCLUSIONS

1. The reaction rate of oxidation of the aldehyde methyl group in substituted toluenes by atmospheric oxygen in the presence of Fe or Cu powder using acetone or pyridine as the solvent is weakly dependent on the nature of the substituent.

2. As a test of selectivity in activation of the C-H bond it is possible to use the ratio of oxidation rates in the toluene molecule (ring C-H bond)/(C-H bond in the  $\text{CH}_3$  group) and the ratio of oxidation rates for  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}/\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ .

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