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New Catalysts for the Conversion of Cumene Hydroperoxide into Phenol

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Abstract: Several copper and iron salts are good catalysts for the conversion of cumene hydroperoxide into phenol. © 1997 Published by Elsevier Science Ltd.

The conversion of cumene hydroperoxide into phenol under acidic conditions, is an important industrial process.¹ In the recent patent literature, new acid based procedures are still reported.^{2.3}

The conversion of cumene hydroperoxide into acetophenone and cumyl alcohol under the influence of simple copper or iron salts is also a well known phenomenon.^{4.5} There are not many examples of metal catalysed reactions where phenol is formed,^{3.6} and relatively high temperatures are often involved.

We first studied the reaction of cumene hydroperoxide with $Cu(ClO_4)_26H_2O$ in acetonitrile (30 mL), expecting to see fragmentation into acetophenone and methyl radicals. However, the product was phenol⁷ in high yield (**Table 1**).

→ → → → →	Cu ^a	OH OH	Yield %	t _{1/2}	Turn over
0.50	0.50	0.41	82	60'	0.82
1.00	0.10	0.925	92.5	30'	9.25
1.00	0.05	0.89	89	20'	17.8
5.39	0.10	4.52	80	45'	45.2

<u>Table 1</u>: Formation of phenol in presence of $Cu(ClO_4)_2 6H_2O$

The solvent acetonitrile has a major influence on the reaction. The addition of pyridine (2mL) or water (2 mL) completely inhibits the reaction. Likewise, ethanol and THF as solvents behaved in the same way.

The fragmentation of cumene hydroperoxide was especially efficient and fast with a variety of iron salts (**Table 2**). The reactions were carried out at room temperature, but decreasing the temperature to 0° C also permitted fast reactions ($t_{1/2}$ about 30 min).

	ОН	
iron salts	\bigcirc	half life $(t_{1/2})$
Fe(ClO ₄) ₃ n H ₂ O	1.01	< 5 min
FeCl ₃	1.0	< 5 min
$Fe(ClO_4)_2$	1.1	< 5 min
FeCl ₃ 2 CH ₃ CN ⁸	0.97	< 5 min

Table 2: Decomposition of the hydroperoxide with different iron salts.

Cumene hydroperoxide 1 mmol, iron salt 0.1 mmol, CH₃CN 30 mL at room temperature.

Using Fe^{II} perchlorate, the reaction gave impressive turn-overs of nearly one thousand (**Table 3**).

		•			_
Fe ^m	°+⊖	OH OH	yield %	Turn over	_
0.10	1.0	0.91	91.0	9.1	-
0.01*	1.08	1.04	95.6	104	
0.10	9.29	8.61	92.7	86.1	
0.01*	10.2	9.31	91.0	931	

<u>Table 3</u>: Use of catalytic amount of $Fe^{III}(ClO_4)_3$ nH₂O

* A solution of iron salt (0.01 mmol) in acetonitrile was prepared (25 mL). I mLof the previous solution is added to the cumene hydroperoxide

in solution in 29 mL of acetonitrile.

The volume of solvent could be decreased to 10 mL of acetonitrile. With less solvent, the reaction is exothermic and even explosive (Table 4, entries 8 and 9), and the yields decreased.

Other solvents were also examined. Methylene dichloride was comparable to acetonitrile and toluene also gave an excellent yield of phenol.

Fe ^m	°+⊖ ⊖	CH3CN	OH OH	Yield %	Turn over
$Fe(ClO_4)_3nH_2O$		1	ille for for south a regard of agent and a summalifier fo		
0.01 mmol	1.08 mmol	30 mL	1.04 mmol	96.3	104
Fe(ClO ₄) ₃ nH ₂ O		1			
0.01 mmol	1.10 mmol	10 mL	1.01 mmol	91.8	101
Fe(ClO ₄) ₃ nH ₂ O					
0.01 mmol	1.00 mmol	5 mL	0.92 mmol	92	92
Fe(ClO ₄) ₃ nH ₂ O					
0.01 mmol	10 mmol	30 mL	9.31 mmol	93.1	931
Fe(ClO ₄) ₃ nH ₂ O					
0.01 mmol	10 mmol	10 mL	9.63 mmol	96.3	963
FeCl ₃		1			
0.01 mmol	1.00 mmol	1 mL	0.94 mmol	94	94
FeCl ₃ 2 CH ₃ CN					
0.01 mmol	1.00 mmol	1 mL	0.88 mmol	88	88
FeCl ₃ 2 CH ₃ CN					
0.01 mmol	5.00 mmol	1 mL	0.27 mmol	5.4	27
FeCl ₃ 2 CH ₃ CN					
0.01 mmol	1 mmol	0 mL	0.17 mmol	17	17
	Fe^{III} $Fe(ClO_4)_3nH_2O$ 0.01 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol $FeCl_3$ 0.01 mmol $FeCl_3$ 2 CH_3CN 0.01 mmol $FeCl_3$ 2 CH_3CN 0.01 mmol $FeCl_3$ 2 CH_3CN 0.01 mmol $FeCl_3$ 2 CH_3CN 0.01 mmol	Fe^{II} re^{OH} $Fe(ClO_4)_3nH_2O$ 0.01 mmol 0.01 mmol 1.08 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol 0.01 mmol 1.10 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol 0.01 mmol 1.00 mmol $Fe(ClO_4)_3nH_2O$ 0.01 mmol $FeCl_3 2 CH_3CN$ 0.01 mmol 0.01 mmol 1.00 mmol $FeCl_3 2 CH_3CN$ 0.01 mmol 0.01 mmol 5.00 mmol $FeCl_3 2 CH_3CN$ 0.01 mmol 0.01 mmol 1 mmol	Fe^{III} $O^{IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$	Fe^{III} OH OH OH $Fe(ClO_4)_3nH_2O$ OOH OH OH 0.01 mmol 1.08 mmol 30 mL 1.04 mmol $Fe(ClO_4)_3nH_2O$ OOH OOH $IO \text{ mmol}$ $IO \text{ mmol}$ 0.01 mmol 1.10 mmol $IO \text{ mL}$ IOH IOH $Fe(ClO_4)_3nH_2O$ $IO \text{ mmol}$ $IO \text{ mL}$ IOH $OOI \text{ mmol}$ $I.00 \text{ mmol}$ 5 mL $O.92 \text{ mmol}$ $Fe(ClO_4)_3nH_2O$ $OO \text{ mmol}$ $IO \text{ mL}$ 9.31 mmol $Fe(ClO_4)_3nH_2O$ $IO \text{ mmol}$ $IO \text{ mL}$ 9.63 mmol $Fe(ClO_4)_3nH_2O$ $IO \text{ mmol}$ $IO \text{ mL}$ 9.63 mmol $Fe(ClO_4)_3nH_2O$ $IO \text{ mmol}$ $IO \text{ mL}$ 9.63 mmol $FeCl_3 2 CH_3CN$ $I \text{ mL}$ 0.94 mmol $FeCl_3 2 CH_3CN$ $O.01 \text{ mmol}$ $I.00 \text{ mmol}$ $I \text{ mL}$ 0.27 mmol $FeCl_3 2 CH_3CN$ $I \text{ mmol}$ $I \text{ mL}$ 0.17 mmol 0.01 mmol $I \text{ mmol}$ $I \text{ mL}$ 0.17 mmol	Fe^{III} OH OH OH OH $Fe(ClO_4)_3nH_2O$ OOI $OOII$ $OOII$ $OOII$ $OOII$ $OOII$ $OOII$ $OOIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$

Table 4: Variation of the amount of solvent

In the fragmentation of cumene hydroperoxide, the second product is acetone. It would, therefore, be advantageous to use this solvent for the reaction. As shown in **Table 5**, the reaction proceeds in acetone more slowly than in acetonitrile, but the yields are comparable. If 0.1 mmol of ferric chloride is added in acetone, then the $t_{1/2}$ returns to 5 minutes.

Volume of acetone (x)	phenol	t _{1/2}	Yield %	Turn over
3 mL	0.89	45'	98.05	89
5 mL	0.96	60'	98.9	96
10 mL	0.95	60'	91	95

Table 5: amount of acetone

Cumene hydroperoxide 1 mmol, FeCl, 0.01 mmol, Acetone x mL, at room temperature.

This method is an efficient way to produce phenol from the cumene hydroperoxide under mild conditions. Actually, 1 mmol of the cumene hydroperoxide is converted into phenol with 100% yield in the following simple and mild conditions: 0.1 mmol of FeCl₂ in 5 ml of acetone, at room temperature, in less than 5 minutes.

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7 - In order to prove that the product was really phenol, a derivative from 2,4-dinitrobenzoic acid was synthetized and compared with an authentic sample. To 30 mL of acetonitrile containing 0.1 mmol of Fe(ClO,),nH,O, cumene hydroperoxide (10.4 mmol) was added. At the end of the reaction, the mixture was poured into a saturated solution of NaHCO, and extracted with ether. The organic phases were dried over MgSO₄, filtered and concentrated by rotavapor. The product obtained was put in solution with dicyclohexyl carbodiimide (1.05 eq) in anhydrous THF (30 mL) at 0°C. 2,4-Dinitrobenzoic acid (1 eq) in solution in THF was added dropwise. The reaction mixture was stirred overnight at room temperature. The precipitate was filtered over silica. The filtrate was concentrated by rotavapor. The residue was recrystallised twice from hot methanol. Yellow crystals were obtained: yield, 90% (crude), 29 % (recrystallised); mp= 123-129°C, 'H NMR (CDCl₃), 8.89 (d, 1H), 8.575 (d, 1H), 8.05 (d, 1H), 7.22-7.45 (m, 5H); ¹³C NMR (CDCl₃), 119.86, 120.957, 126.9, 127.952, 129.79, 131.415, 132.5, 150.019, 162.238; IR (KBr) 1745.66 cm-1 (Y (---)).

The authentic sample prepared in the same way, from the commercial phenol, give a yellow crystalline compound with the same caracteristics. The mixed melting point of the two products was 122-130°C.

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