

Cation Radicals: Aromatic Chlorination *via* Peroxydisulphate – Copper(II) Chloride Systems

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Summary Aromatic cation radicals, produced by oxidation of benzene and toluene with peroxydisulphate ion in water–acetonitrile mixtures, are efficiently trapped by copper(II) chloride with formation of moderate to good yields of ring chlorinated products; in contrast, side chain chlorination of toluene occurs when copper(II) chloride is replaced by chloride ion.

It is well known that copper(II) salts react extremely rapidly with organic free-radicals and detailed mechanisms of these interactions are now clearly established.¹ We now report results which indicate that copper(II) chloride is also a very effective scavenger of organic cation-radicals, providing a novel chlorination procedure for aromatic molecules.

Peroxydisulphate ($S_2O_8^{2-}$) ion is known to act as a one-electron oxidant for suitable organic substrates^{2,3} and work has recently been extended to include formation and

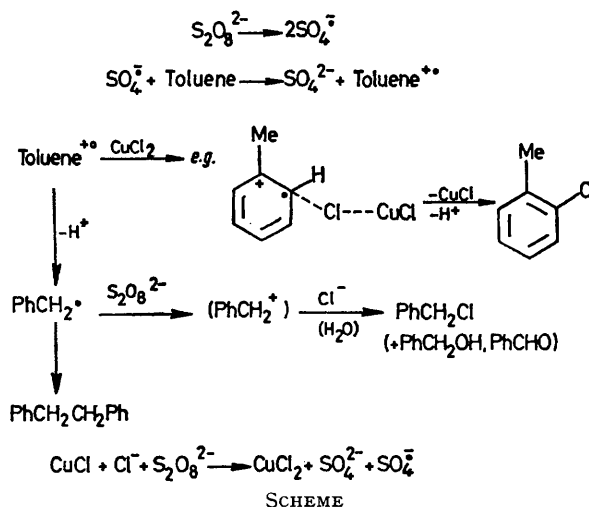


TABLE. Reaction of sodium peroxydisulphate^a with aromatic hydrocarbons in the presence of copper(II) chloride.

Substrate	MeCN : H ₂ O ^b	[CuCl ₂ ·2H ₂ O] M	[LiCl] M	Products ^c (%)
Toluene ^d	4 : 1 ^f	0.02	0.44	Chlorotoluenes (81)
"	4 : 1	—	0.44	PhCH ₂ Cl (85)
"	4 : 1	0.25	—	Chlorotoluenes (60); PhCH ₂ Cl (0.5)
"	4 : 1 ^f	0.25	—	Chlorotoluenes (75)
"	4 : 1 ^f	0.48	—	Chlorotoluenes (85)
Benzene ^e	1 : 4 ^f	0.02	1.15	PhCl (60) ^g
"	1 : 4	0.21	0.76	PhCl (25)
"	4 : 1	0.18	—	PhCl (15)
"	4 : 1	—	0.40	PhCl (0); ClCH ₂ CN (<i>ca.</i> 20)
"	1 : 4	0.21	—	PhCl (5) ^h

^a $[Na_2S_2O_8] = 5.0 \times 10^{-2} M$; reactions taken to complete loss of peroxydisulphate, usually 3 h at 60–85°. ^b v/v. ^c Products analysed by g.l.c. of the ether-extracted reaction mixtures; g.l.c.–m.s. used for further identification and i.r. spectroscopy was also used in the evaluation of the isomeric chlorotoluenes. ^d 0.20 M. ^e 0.22 M. ^f HCl added, 0.2 M. ^g The yield of PhCl was increased further in the presence of a greater concentration of chloride ion. ^h In reactions yielding small amounts of PhCl polymeric resin was also produced.

trapping of cation radicals from pyridine in aqueous solution.⁴ On heating aqueous–acetonitrile solutions containing benzene, sodium peroxydisulphate, and copper(II) chloride, a moderate to good yield of chlorobenzene is obtained depending on the precise conditions employed (Table). Control experiments showed the absence of chlorobenzene formation when the peroxydisulphate was omitted.⁵ Only a catalytic amount of copper chloride is needed and the reaction can be carried out in a predominantly aqueous solution providing there is an excess of chloride ion; acid is apparently beneficial to the yields of nuclear chlorinated hydrocarbon produced.

Mechanistic information is provided when toluene is chlorinated using the same procedure (Table). In this case yields of chlorinated product are higher, and very good yields of entirely nuclear substituted chlorotoluenes are formed on heating aqueous–acetonitrile solutions of toluene, $Na_2S_2O_8$, hydrochloric acid, and copper(II) chloride. The yield is unaffected by dissolved oxygen (air) and no benzyl

chloride or other organic products are formed (g.l.c.). In marked contrast, in the absence of copper chloride, but in the presence of lithium chloride a very good yield of benzyl chloride is produced to the exclusion of nuclear substituted products, showing the dramatic effect of the copper(II) salt on the course of reaction. Furthermore, in the absence of both copper(II) and chloride ions, heating aqueous–acetonitrile solutions of $S_2O_8^{2-}$ and toluene produced a mixture of bibenzyl (50%), benzyl alcohol (10%), and benzaldehyde (30%).⁶

The results are accommodated by the mechanism in the Scheme.

Formation of good yields of benzyl chloride when chloride [but not copper(II)] ions are present, and of bibenzyl when they are omitted, is consistent with results from other oxidants which show that oxidation of benzyl radicals is easily effected in the presence of transferable ligands such as chloride ion.⁷ A possible mechanism in this and other systems involves formation of benzyl chloride anion radical

(PhCH_2Cl^-) with subsequent oxidation by $\text{S}_2\text{O}_8^{2-}$ or other oxidants.

The isomer distribution of chlorotoluene products (58% *ortho*, ca. 4% *meta*, ca. 38% *para*) provides important support for the mechanism proposed for nuclear chlorination of aromatic cation radicals by copper(II) chloride since, allowing for the statistical factor, it follows the known order of spin densities (*para* > *ortho* > *meta*) in toluene cation radical.⁸ Other activated substituted benzenes and condensed aromatic molecules react with $\text{S}_2\text{O}_8^{2-}$ - CuCl_2 systems in a similar manner to give the anticipated chlorinated products and details will be given in the full paper.

Extensive studies by Kochi^{1,9} have established that trapping of organic radicals by copper(II) derivatives occurs at essentially diffusion-controlled rates; the present data, together with the recently reported scavenging of pyridine cation-radicals by phenyl t-butyl nitron,⁴ indicate that cation radicals may be similarly easily trapped at the radical site.

Solvent mixtures employed in the present work were

chosen for convenience rather than for optimisation of product yields and it is clear that the reactions may be effected in water or predominantly aqueous organic solvents providing that solubility and/or dispersion of organic substrate and products in water are adequately taken into account, and that the copper(II):chloride:solvent ratios are adjusted to ensure formation of the yellow-green CuCl_4^{2-} ion.¹⁰

Aromatic cation radicals are now fairly commonly invoked as reaction intermediates in metal-catalysed¹¹ and anodic-oxidative¹² substitution processes, and there have been several reports of mixed products arising from trapping by added nucleophiles such as Cl^- , CN^- , NO_2^- , and pyridine.¹³ The present data suggest that aromatic cation radicals derived from any source should be trapped by copper(II) salts to give specific ring substitution products and such studies are now in progress.

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