A New Mechanism for Peroxydisulphate-initiated, Copper-mediated, Aromatic Halogenation

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Summary The peroxydisulphate ion oxidises the halide ion to molecular halogen which reacts with mesitylene in the presence of Cu^{II}, to yield halogenomesitylene; when Cu^{II} is absent, side-chain products are formed predominantly.

Ledwith and Russell have recently reported the nuclear chlorination of aromatics using peroxydisulphate as initiator.[1] Their system consisted of sodium peroxydisulphate, lithium chloride, copper(II) chloride, hydrochloric acid, water, acetonitrile, and organic substrate. We have observed similar results using a system previously reported for iodination,[2] consisting of potassium peroxydisulphate, potassium chloride, copper(II) sulphate, water, and mesitylene as the primary organic substrate.

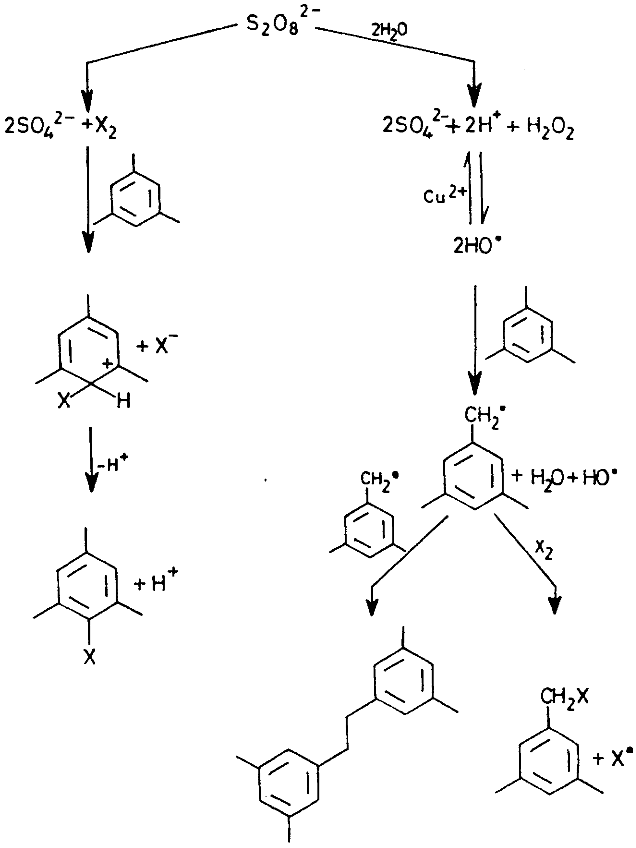
In the mechanism previously proposed[1] the peroxydisulphate ion oxidises the aromatic substrate to generate a cation radical, which is the reactive species. Catalytic amounts of co-ordinated copper(II) act as the source of halogen and the observed reactivity towards nuclear chlorination increases in the order toluene < *m*-xylene < mesitylene, consistent with the expected relative stabilities of the cation radicals.

After detailed study of the halogenation of mesitylene by this reaction, we conclude that (a) there is no evidence for participation of cation radicals and that the aromatic hydrocarbon is the reactive substrate; (b) molecular halogen, rather than CuX_2, is the halogenating agent; and (c) the role of Cu^{II} is to mitigate the otherwise preponderant side-chain halogenation.

Consideration of the standard reduction potentials[3] of peroxydisulphate, chloride, bromide, and iodide ions leads to the prediction that peroxydisulphate oxidises these halides, but not fluoride ion, to the corresponding molecular halogens. This was confirmed by generation of the free halogen when potassium halide and $K_2S_2O_8$ were heated in water. In the presence of mesitylene and Cu^{II}, halogenomesitylene was obtained in high yields. The role of molecular halogen was clearly established by trapping experiments in which cyclohexene was added to the reaction mixture. No chloromesitylene could be isolated. Instead, 1,2-dichlorocyclohexane and 2-chlorocyclohexanol were formed.

We observed, moreover, that reactivity towards nuclear halogenation is consistent with the order expected on the basis of the stabilities of σ complexes,[4] *viz.*, toluene < *m*-xylene < mesitylene. Since fluoride, cyanide, and acetate failed to give any ring-substituted compounds, products which would be expected if cation radicals are intermediates, we can only conclude that the aromatic hydrocarbon reacts directly with molecular halogen.

When Cu^{II} sulphate was omitted from our system, mesitylene was converted predominantly to the coupling product, 1,2-bis(3,5-dimethylphenyl)ethane with lesser amounts of 3,5-dimethylbenzyl chloride and chloromesitylene. These results strongly suggest that the role of Cu^{II} is to prevent the formation of the organic radicals that lead to side-chain products. It is known[5] that Cu^{II} intercepts radicals such as ·OH which would be necessary to initiate the generation of the organic radical. More than catalytic amounts of Cu^{II} are required to suppress completely formation of side-chain products.



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On the basis of these observations, we propose the mechanism depicted in the Scheme. Details of these experiments will be presented in the full paper.

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