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THE MECHANISM OF ELECTROPHILIC SIDE-CHAIN SUBSTITUTIONS OF POLYALKYLBENZENES. ARGUMENTS AGAINST THE ELECTRON TRANSFER PATHWAY[1]

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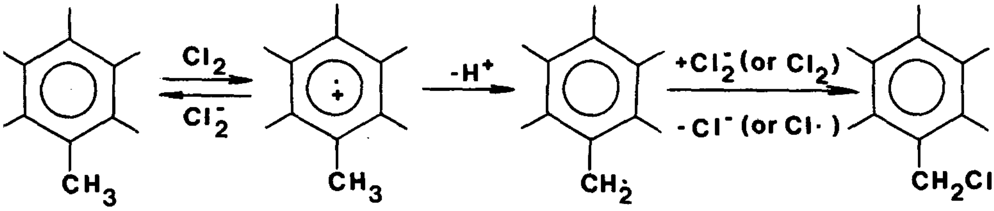
Lately Kochi has made the interesting discovery that when chlorine and hexamethylbenzene are mixed in acetic acid hexamethylbenzene cation radical is formed at room temperature.[2] On the basis of this finding Kochi has suggested that the side-chain chlorination of alkyl aromatics under electrophilic conditions (as well as other similar reactions) may proceed by the electron transfer mechanism shown in scheme I.



Scheme I

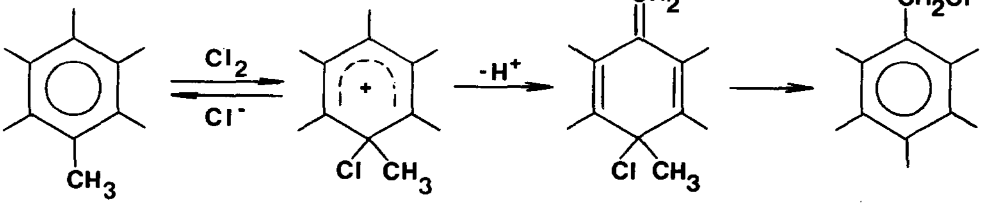
Although this mechanism appears, jn principle, very attractive, we wish to point out that it is not consistent with product distribution, positional selectivity and orientation exhibited by the electrophilic side-chain chlorination of methylbenzenes.

In the first place, the scheme suggested by Kochi does not account for the formation of substantial amounts of benzyl acetates which accompanies that of the side-chain chlorinated products.[3,4,5] These acetates do not derive from the solvolysis of previously formed benzyl chlorides, but share with the chlorides a common reaction intermediate.

In the second place, on the basis of scheme I, the electrophilic side-chain chlorination should be characterized by a small positional selectivity, mainly determined by the relative stability of the free radicals formed by the radical cation. This conclusion is supported by the recent observation[6] that in the reaction of Ce(IV) with isodurene in acetic acid (a reaction which presumably involves the formation of a radical cation[7]) all the three isomeric benzyl acetates are obtained, 2,4,6-trimethylbenzyl acetate being that formed in the largest amount.

In contrast, side-chain chlorination of isodurene exhibits an extremely high positional selectivity since only one of the possible isomers is formed, 3,4,5-trimethylbenzyl chloride.[5] More significantly, this isomer is not the one deriving from the most stable radical among those which can be obtained from the isodurene radical cation.

Whereas these findings cannot be explained by scheme I they perfectly fit the heterolytic mechanism proposed, on the basis of several pieces of evidence[3,5] for the side-chain chlorination of alkyl aromatics. According to this mechanism (scheme II) side-chain substitution is predicted to occur at the



Scheme II

position _para_ to that attacked by the electrophile and this has indeed been observed in the side-chain chlorination of isodurene[5] and in the side-chain nitration of several polymethylbenzenes.[8] Moreover we have obtained good evidence that rearrangement of the cyclohexadiene intermediate to the side-chain substituted product takes place _via_ ion pair formation;[9] thus, an exchange of the ion pair with the solvent acetic acid may easily account for the presence of benzyl acetates in the reaction product.

In conclusion the mere detection of hexamethylbenzene radical cation in the reaction mixture does not seem sufficient to support scheme I as a possible, major pathway for the side-chain electrophilic reactions.[10]

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7. Preliminary experiments have shown that the rate of oxidation of methylbenzenes by Ce(IV) is extremely sensitive to the number of the methyl groups in the ring. For example the reactivity ratio hexamethylbenzene/isodurene is ~1600. This observation strongly supports the formation of a radical cation in the rate determining step.
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