Aromatic Chlorination by Peroxodisulphate and Chloride Ions. Cation Radical Trapping by Copper(II) Chloride

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Details are presented of the factors governing chlorination of aromatic molecules *via* formation of the corresponding cation radicals, produced by peroxodisulphate oxidation. Moderately stable cation radicals (*e.g.* from naphthalene or anisole) react directly with chloride ion to give quantitative yields of mononuclear chlorinated hydrocarbon. With less reactive substrates (*e.g.* benzene, toluene) no nuclear chlorination occurs, although with the latter high yields of side-chain chlorinated product are obtained. For polymethylated benzenes (xylenes, mesitylene), nuclear or side chain chlorination occurs according to the relative stabilities of the aromatic cation radical and the corresponding benzylic radical formed by deprotonation. Side-chain chlorination is thought to involve coupling of benzylic radicals with chloride ion. Catalytic amounts of copper(II) chloride dramatically change the reaction course giving entirely ring chlorinated products and it is proposed that copper(II) chloride is a highly efficient scavenger of aromatic cation radicals.

DETAILED results from a recent study of the reactions between peroxodisulphate ion and pyridine established the formation and subsequent involvement in a chain reaction of the pyridine cation radical.[1] Earlier it was demonstrated [2,3] that alcohol oxidations by peroxodisulphate ion involved primary one electron transfer processes between the alcohol and $SO_4^{\overset{\cdot}{-}}$, the latter arising from homolytic decomposition of the peroxo-compound. In preliminary communications [4,5] evidence has been presented for similar electron transfer oxidations of benzene and other aromatic molecules and for all the aromatic substrates investigated the primary process can be represented as (1). We have shown that aromatic cation radicals so generated react with chloride ion to give nuclear and side-chain chlorination products and a most important result is the dramatic directing effect of catalytic amounts of copper(II) chloride, leading to exclusive nuclear substitution.[4] These processes have relevance to the peroxodisulphate-initiated emulsion polymerisation of styrene and related monomers.[6]

$$ArH + SO_4^{\overset{\cdot}{-}} \longrightarrow (ArH)^{+\cdot} + SO_4^{2-} \qquad (1)$$

RESULTS AND DISCUSSION

The initial studies of oxidation by peroxodisulphate ion in essentially aqueous solutions involved alcohol substrates [2,3] and lead to a reaction mechanism exemplified by the case of methanol (Scheme 1).

$$\begin{gathered}
S_2O_8^{2-} \xrightarrow{\text{heat}} 2SO_4^{\overset{\cdot}{-}} \\
MeOH + SO_4^{\overset{\cdot}{-}} \longrightarrow MeOH^{+\cdot} + SO_4^{2-} \\
MeOH^{+\cdot} \xrightarrow{-H^+} Me\dot{O} \xrightarrow{MeOH} \dot{C}H_2OH \xrightarrow{S_2O_8^{2-}} CH_2{=}O
\end{gathered}$$

SCHEME 1

In support of this mechanism oxidation of 2-phenylethanol and related compounds [3,7] gave products indicating fragmentation of alkoxyl radicals (Scheme 2).

$$\begin{tikzcd}
PhCH_2C(OH)R^1R^2 \arrow[r, "SO_4^{\overset{\cdot}{-}}", "-(HSO_4^-)"'] & PhCH_2C(O\cdot)R^1R^2 \arrow[d] \\
(PhCH_2)_2 & Ph\dot{C}H_2 + R^1R^2C{=}O \arrow[l]
\end{tikzcd}$$

SCHEME 2

In an extension of this work the effects of copper(II)

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[1] A. Ledwith and P. J. Russell, *J.C.S. Perkin II*, 1974, 582.

[2] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *Chem. Comm.*, 1971, 964; *Proc. Roy. Soc.*, 1973, *A*, **332**, 151.

[3] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 630.

[4] A. Ledwith and P. J. Russell, *J.C.S. Chem. Comm.*, 1974, 291.

[5] A. Ledwith and P. J. Russell, *J.C.S. Chem. Comm.*, 1974, 959.

[6] A. Ledwith and P. J. Russell, *J. Polymer Sci., Polymer Letters*, 1975, **13**, 109.

[7] M. E. Snook and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1974, **96**, 860; A. Clerici, F. Minisci, and O. Porta, *Tetrahedron Letters*, 1974, 4183.

chloride, an extremely efficient scavenger of carbon-centred radicals such as benzyl,[8] were investigated. Surprisingly the anticipated high yields of benzyl chloride *were not* observed; in each case chlorinated starting material was found to be the major product. Typically, oxidation of $PhCH_2C(OH)Me_2$ by peroxodisulphate ion gave the products indicated in Table 1. Clearly both chloride ion and especially copper(II) chloride have a marked effect on the nature of reaction products. In an attempt to rationalise these observations, a more detailed study of the reactions of aromatic cation radicals with Cl^- and $CuCl_2$ was undertaken.

TABLE 1

Reaction between sodium peroxodisulphate and $PhCH_2C(OH)Me_2$ [a]

Additive	Products (%)
None	Bibenzyl 75
LiCl [b]	Bibenzyl 8 Benzyl chloride 70
LiCl [b] + $CuCl_2$ [c]	Bibenzyl <1 Benzyl chloride 10 Nuclear chlorinated alcohols [d] 65

[a] $[Na_2S_2O_8]$ = 0.05M; $PhCh_2C(OH)Me_2$ 0.15M; in 4 : 1 v/v acetonitrile–water at 80°. [b] [LiCl] = 0.3M. [c] $[CuCl_2,2H_2O]_0$ = 0.05M. [d] Isomer mixture not characterised but identified qualitatively by g.l.c.–mass spectrometry.

TABLE 2

Reaction of sodium peroxodisulphate [a] with aromatic hydrocarbons in the presence of lithium chloride [b]

	Monochlorohydrocarbon products [c]	
Substrate	Side chain (%)	Nuclear (%)
Toluene	100	0
p-Xylene	100	0
m-Xylene	90	10
Mesitylene	25	75

[a] $[Na_2S_2O_8]_0$ = 0.05M; solvent 4 : 1 v/v MeCN–H_2O; reactions at 80° for 3.0 h in the presence of 0.2M-HCl. [b] [LiCl] = 0.3M. [c] G.l.c. analysis of ether extracted solutions; g.l.c.–mass spectrometry used for further identification.

TABLE 3

Reaction of sodium peroxodisulphate [a] with benzene.[b] Variation of reaction conditions

[Benzene]/M	MeCN : H_2O (v/v)	Temp. (°C)	Time (h)	$[CuCl_2,2H_2O]$/M	[LiCl]/M	Other additives	% PhCl obtained [c]
0.22	1 : 4	80	3	0.02	1.15	0.2M-HCl	60 [d]
0.22	1 : 4	80	3	0.02	1.35		48
0.22	1 : 4	80	3	0.21	0.76		25
0.02	1 : 4	80	3	0.02	1.15	0.2M-HCl	60 [e]
0.02	1 : 4	80	3	0.21			5
0.22	4 : 1	80	3	0.18			15
0.22	4 : 1	40	3	0.18			1
0.22	4 : 1	80	3		0.40		0 [f]

[a] $[Na_2S_2O_8]_0$ = 0.05M. [b] Distilled AnalaR benzene made no difference. [c] By g.l.c. using internal standard method. [d] The yield of PhCl is increased further in the presence of a greater concentration of chloride ion. [e] Some dichlorobenzene was also formed, see Table 4. [f] Polymeric resin was the major product.

Chlorination by Peroxodisulphate–Chloride Ion.—The reactions of a series of aromatic compounds with sodium peroxodisulphate in the presence of lithium chloride were investigated in water–acetonitrile solvent. Benzene yielded no chlorobenzene and gave only trace amounts of other (unidentified) organic products. However, naphthalene gave a 90% yield of chloronaphthalene isomers. Other activated benzene derivatives such as anisole and phenol likewise gave high yields of nuclear chlorinated hydrocarbon. Thus monochlorinated derivatives were obtained from anisole (*para* + *meta* 75%, *ortho* 25%), phenol (*para* + *meta* 50%, *ortho* 50%) and naphthalene (mixture of 1- and 2-) in essentially quantitative yields when the aromatic molecules were allowed to react with $Na_2S_2O_8$ and LiCl in water–acetonitrile solution. In contrast, deactivated derivatives (chlorobenzene, nitrobenzene) did not yield significant amounts of identifiable products.

Corresponding reactions with methyl substituted benzenes gave results as shown in Table 2 which are of mechanistic value. In the absence of chloride ion, reactions of methylbenzenes with peroxodisulphate give mixtures of oxidation products.[9] For example, toluene in aqueous acetonitrile gave bibenzyl (50%), benzaldehyde (30%), and benzyl alcohol (10%). On addition of lithium chloride to the toluene-containing reaction mixtures, benzyl chloride (85%) was the major product. Related side chain chlorination was observed for reactions of *p*-xylene but *m*-xylene and mesitylene gave increasing amounts of nuclear chlorinated products (Table 2).

Chlorination by Peroxodisulphate–Copper(II) *Chloride.*—On heating aqueous acetonitrile solutions containing benzene, sodium peroxodisulphate, and copper(II) chloride, a moderate to good yield of chlorobenzene was obtained depending on the precise conditions employed (Table 3). Control experiments showed the absence of chlorobenzene formation when peroxodisulphate was omitted. 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.

A further series of experiments was directed towards defining the scope of the reaction. Substrates more reactive (electron rich) than benzene reacted faster and gave higher yields of chlorinated products. Thus toluene gave >80% yields of chorotoluenes and over 90% yields were obtained with anisole, naphthalene,

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[8] J. K. Kochi, 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 1, ch. 11.

[9] R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.*, 1960, 1332.

xylenes, *etc.* In all cases the aromatic substrate gave entirely nuclear substituted chlorinated products on reaction with peroxodisulphate ion and a catalytic amount of $CuCl_2$ (Table 4). Although side chain chlorination was, in principle, an alternative pathway with methylbenzenes no such reactions occurred.

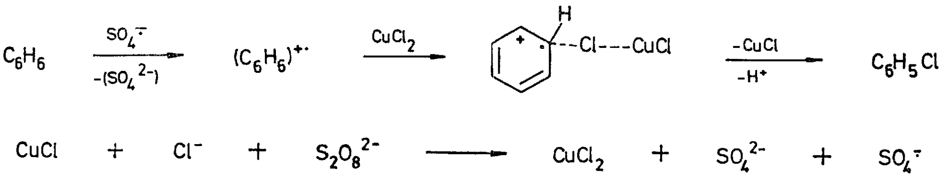
TABLE 4

Reaction of sodium peroxodisulphate[a] with aromatic hydrocarbons[b] in the presence of chloride ion[c] and a catalytic amount of $CuCl_2$ in 4 : 1 v/v acetronitrile–water solution[d]

	Products (%)[e]
Benzene	PhCl (30)
Toluene	Chlorotoluenes (80; 58% *ortho, ca.* 4% *meta, ca.* 38% para.)
Chlorobenzene	Dichlorobenzene (18; 40% *ortho,* 5% *meta,* 55% *para.*)
Anisole	Chloroanisoles (86; *ortho* 25%, *para* + *meta* 75%)
p-Xylene	Monochloro-*p*-xylene (92)
Mesitylene	Monochloromesitylene (95)
Naphthalene	1- and 2-chloronaphthalenes (85)
Phenol	Chlorophenols (90; *ortho, ca.* 50%, *para* + *meta, ca.* 50%)

[a] $[Na_2S_2O_8]_0 = 0.05$M. [b] $[\text{Hydrocarbon}]_0 \sim 0.15$M. [c] Lithium chloride (0.3M) and hydrochloric acid (0.2M) were present. [d] Reactions carried out at 80° for 3.0 h, in the presence of 0.02M-$CuCl_2,2H_2O$. [e] G.l.c. analysis of ether extracted reaction mixtures.

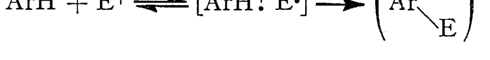
Reaction Mechanisms.—The enhanced reactivity of activated benzenes towards peroxodisulphate ion is consistent with a primary one electron transfer process [equation (1)]. From the results presented it would follow that, in the presence of catalytic amounts of copper (II) chloride, aromatic cation radicals react with chloride ion to give exclusively ring-substituted products. In the absence of $CuCl_2$ the aromatic cation radical participates in competing processes leading to both side chain and nuclear chlorination according to the nature and position of substituents.



SCHEME 3

We suggest that the catalytic role of copper(II) chloride in directing selective aromatic nuclear chlorination arises from efficient trapping of the substrate cation radical (Scheme 3). Extensive studies by Kochi[8,10] 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-butylnitrone[1] indicate that cation radicals may be similarly easily trapped at the radical site.

Product distributions of chlorotoluenes (58% *ortho, ca.* 4% *meta, ca.* 38% *para*) and dichlorobenzenes (40% *ortho,* 5% *meta,* 55% *para*) together with the partial resolution of the other chlorinated aromatic hydrocarbons indicates that the isomer distribution is similar to that obtained in conventional electrophilic substitution.[11] However, these isomer distributions follow the known order of spin densities in the aromatic cation radical (*e.g.* $p > o > m$ for toluene[12]) consistent with the proposed cation radical trapping mechanism. It is interesting to note that current theories of certain electrophilic aromatic substitutions[13-15] include the possibility of an electron transfer mechanism (2). In this case the new bond is formed between E· and the carbon atom of the cation radical $ArH^{+\cdot}$ with the highest unpaired electron density. Scavenging of an aromatic cation radical by copper(II) choride would be anticipated to take place at the same carbon atom in view of its very high reactivity with carbon radicals.[10,16]



$$ArH + E^+ \rightleftharpoons [ArH^{+\cdot}\,E\cdot] \longrightarrow \left(Ar\begin{matrix}H\\E\end{matrix}\right)^+ \qquad (2)$$

A similar mechanism for nuclear halogenation of highly reactive aromatic molecules by copper(II) halides had originally been suggested by Nonhebel and his collaborators[17] although here the role of copper(II) (primary oxidant) is considerably more complex than in the present work, and the reaction conditions are very different. Nuclear hydroxylation of aromatics by Fenton's reagent is catalysed by copper(II) salts[18a] and it is possible that the copper(II) chloride induced chlorination of olefins[18b] may also have related mechanistic features.*

Throughout this work it was observed that isomer distributions for ring chlorinated products were identical for copper(II) catalysed processes and (where appropriate) for reactions with $S_2O_8^{2-}$–Cl^- only. Reaction mechanisms

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* Since this manuscript was submitted a paper (C. Walling and D. M. Camaioni, *J. Amer. Chem. Soc.*, 1975, **97**, 1603) has appeared giving details of a related effect of copper(II) on peroxodisulphate-promoted hydroxylation of aromatic molecules.

[10] C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, 1971, **36**, 3103.

[11] P. B. De La Mare and J. H. Ridd, 'Aromatic Substitution, Nitration and Halogenation,' Butterworths, London, 1959.

[12] T. Komatsu, A. Lund, and P.-O. Kinell, *J. Phys. Chem.*, 1972, **76**, 1721.

[13] E. B. Pedersen, T. E. Petersen, K. Torssell, and S.-O. Lawesson, *Tetrahedron*, 1973, **29**, 579.

[14] N. D. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 3188.

[15] J. K. Kochi, R. T. Tang, and T. Bernath, *J. Amer. Chem. Soc.*, 1973, **95**, 7114.

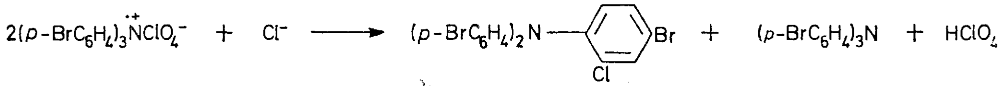
[16] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 856.

[17] See for example S. R. Bansal, D. C. Nonhebel, and J. M. Mancilla, *Tetrahedron*, 1973, **29**, 993.

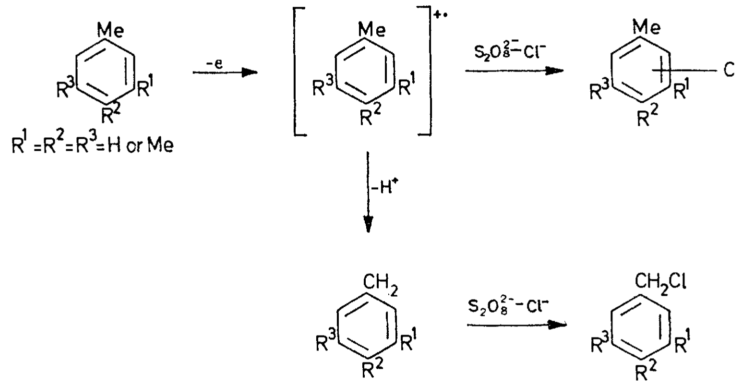
[18] (*a*) C. Walling and R. A. Johnson, *J. Amer. Chem. Soc.*, 1975, **97**, 363; (*b*) A. Or, M. Levy, M. Asscher, and D. Vofsi, *J.C.S. Perkin II*, 1974, 857.

for the latter type of chlorination are still largely speculative (see below) but the difference in reactivity of benzene on the one hand and naphthalene and other activated benzenes with the $S_2O_8^{2-}$–Cl^- mixture in the absence of copper(II) chloride suggested the possibility that aromatic nuclear chlorination by peroxodisulphate and chloride ion was governed by the stability of the initially formed aromatic cation radical. In support of this proposal rapid nuclear chlorination has now been shown to occur when the ammoniumyl salt (1) was allowed to react with added chloride ion in acetonitrile solvent.[19] Similar observations of chloride ion reaction with stable cation radicals have previously been reported by Shine and his co-workers.[20]

Products from chlorination of the various methyl-substituted benzenes (Table 2) indicate a competition of reaction pathway, dependent on cation radical stability, between deprotonation of the intermediate cation radical followed by side-chain chlorination [21] or direct chloride ion capture giving nuclear chlorinated hydrocarbon.



(3)



(4)

(5)

The stability of the cation radicals of substrates in Table 2 would be expected to increase in the order toluene $<$*m*-xylene $<$ mesitylene and yields of nuclear chlorinated product increase from 0—75% in this sequence. In this respect the difference between *m*-xylene and *p*-xylene is particularly significant since the relative stabilization energies of initially formed cation radical, and substituted benzyl radical produced by deprotonation, will differ less for the *meta*-isomer.

These results thus indicate that chloride ion can, under suitable solvent conditions, combine with aromatic cation radicals provided they are relatively stable with respect to those from benzene and toluene.

Exactly how the stabilized aromatic cation radical is converted into the nuclear chlorinated product, and to a lesser extent, how the benzylic radical is converted to the side-chain chlorinated product is not at present fully understood. As represented in equation (4) nucleophilic substitution would arise from initial capture of aromatic cation radical by chloride ion and, although there is a scarcity of significant mechanistic information relating to nucleophilic capture of aromatic cation radicals, in this case, as for every other reported case (*e.g.* for reactions of $ArH^{+\bullet}$ with halide, nitrite, or pyridine [20,22]) the position of substitution corresponds with that arising from comparable electrophilic processes. In this respect it is particularly interesting to note the recently reported [23] preference for *meta*-acetoxylation of aromatic compounds by potassium peroxodisulphate in acetic acid with palladium(II) complexes as catalysts. Here the primary interaction is between palladium(II) and the aromatic molecule and does not, apparently, involve the substrate cation radical.

An alternative mechanism would involve chlorine anion radical ($Cl_2^{\bar{\cdot}}$) as the actual chlorinating species [reactions (6)—(9)]. Reaction (6) could in principle be

$$ArH^{\dot{+}} + Cl^- \longrightarrow ArH + (Cl\cdot) \qquad (6)$$

$$(Cl\cdot) + Cl^- \rightleftharpoons Cl_2^{\bar{\cdot}} \qquad (7)$$

$$Cl_2^{\bar{\cdot}} + ArH^{+\bullet} \longrightarrow ArHCl^+ + Cl^- \qquad (8)$$

$$ArHCl^+ \longrightarrow ArCl + H^+ \qquad (9)$$

replaced by a primary oxidation of Cl^- by $S_2O_8^{2-}$ or $SO_4^{\bar{\cdot}}$ but these reactions are known to be much slower than the corresponding reactions of $SO_4^{\bar{\cdot}}$ with aromatic compounds, due to adverse kinetic factors.[24] On the other hand, an electron transfer reaction between aro-

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[19] J. R. Jackson, Ph.D. Thesis, Liverpool University, 1975.

[20] (*a*) C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, 1971, **36**, 4050; (*b*) H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyana, *ibid.*, 1972, **37**, 2691; (*c*) H. J. Shine and C. V. Ristagno, *ibid.*, p. 3424.

[21] This has recently been well exemplified, J. K. Kochi, *Tetrahedron Letters*, 1975, 41.

[22] U. Svanholm, O. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, 1975, **97**, 101; see also ref. 1 for discussion and further references on nucleophilic capture of aromatic cation radicals.

[23] L. Eberson and L. Jonsson, *J.C.S. Chem. Comm.*, 1974, 885.

[24] (*a*) I. Kraljić, *Internat. J. Radiation Phys. Chem.*, 1970, **2**, 59; (*b*) E. J. Behrman and J. O. Edwards, *Progr. Phys. Org. Chem.*, 1967, **4**, 107.

matic cation radicals and Cl^- would be favoured by electrostatic forces and the standard electrode potentials[25] for the conversion $Cl_2 + 2e = 2Cl^-$ decrease from 1.35 in water to 0.58 V in CH_3CN. It follows that oxidation of Cl^- to ($Cl\cdot$) becomes much more favourable in acetonitrile, and aqueous acetonitriles, and such a process has been demonstrated by Shine and his collaborators[20] for halide ion reactions with perylene cation radical.

The equilibrum constant for formation of $Cl_2^{\cdot-}$ is thought to be high[26,27] and under the conditions used in the present work (high chloride ion concentrations), would ensure that any ($Cl\cdot$) generated, by whatever mechanism, would exist as $Cl_2^{\cdot-}$.

It is important to note that atom transfer from $Cl_2^{\cdot-}$ to $ArH^{+\cdot}$ would obviously occur at the sites of highest spin density, as proposed for the comparable atom transfer from $CuCl_2$, and might have relevance in the mechanisms of more general methods of aromatic chlorination.

The dramatic effects of Cl^-–$S_2O_8^{2-}$ combinations in diverting benzylic radicals from the normal coupling and oxidation processes encountered in oxidation by $S_2O_8^{2-}$, to exclusive formation of benzyl chlorides also calls for a consideration of reaction mechanism. Kochi has shown conclusively that oxidative chlorination of benzyl radical to benzyl chloride is readily accomplished by *ligand* transfer oxidation whereas electron transfer oxidation of benzyl radicals is quite sluggish, even with copper(II) ion.[28] Our observations support this conclusion when benzyl radicals are formed in 1 : 4 v/v water–acetonitrile solutions containing chloride ion and $S_2O_8^{2-}$. There is little evidence for $PhCH_2^+$ formation (benzyl alcohol is not a significant product) and, whilst the relative nucleophilicities of Cl^- and H_2O towards $PhCH_2^+$ are not known for the actual solvent–salt concentrations employed, a more specific oxidative chlorination mechanism, analogous to ligand transfer oxidation, must be considered.

Combination reactions of anions and free radicals are now well enough established from the work of Kornblum,[29] Russell,[30] and Bunnett[31] and the scope of this kind of reaction for simple alkyl radicals has recently been considered.[32]

In all cases the intermediate radical anion is immediately oxidised by some component of the system with formation of neutral substitution product [reaction (10)]. Benzyl radicals, generated in the present work, could

$$R\cdot + X^- \rightleftharpoons [RX]^{\cdot-} \xrightarrow{-e} RX \qquad (10)$$

similarly combine with chloride ion to produce the anion radical of benzyl chloride [reaction (11)]. The equilibrium position of equation (11) would be shifted completely to the right hand side by electron transfer from

$$Ph\dot{C}H_2 + Cl^- \rightleftharpoons [PhCH_2Cl]^{\cdot-} \xrightarrow{S_2O_8^{2-}} PhCH_2Cl + SO_4^{2-} + SO_4^{\cdot-} \qquad (11)$$

$PhCH_2Cl^{\cdot-}$ to $S_2O_8^{2-}$ with concurrent formation of $SO_4^{\cdot-}$ for chain propagation; the reverse reaction involving cathodic reduction of benzyl halides to give benzyl radicals and halide ions is already a well established process.[33]

Role of Solvent.—The solvent system found most useful in this work was 4 : 1 v/v acetonitrile–water. Yields of chlorinated hydrocarbons were highest in the least aqueous solvents, whether or not copper(II) chloride was employed. For the latter systems, the characteristic yellow-green chloride complexes of copper(II) seem to be essential for efficient trapping[16] and increasing water content of the solvent required a corresponding increase in the chloride ion concentration so as to maintain the necessary complex ion equilibria. Chlorocopper(II) complexes are formed readily in acetonitrile and to a very much smaller extent in water. Thus association constants for $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$ are $10^{9\cdot7}$, $10^{7\cdot9}$, $10^{7\cdot1}$, and $10^{3\cdot7}$, respectively, in acetonitrile[34] and only 1.0, 0.2, 0.04, and 0.01, respectively, in water.[35]

Conclusions.—In aqueous acetonitrile solvent, peroxodisulphate ion is a convenient reagent for the generation of cation radicals from aromatic molecules. Copper(II) chloride is a highly efficient scavenger for the cation radicals and, if used in the presence of excess of chloride ion and $S_2O_8^{2-}$, provides a useful process for nuclear chlorination. For aromatic molecules having methyl substituents, the initially formed cation radical, in the absence of $CuCl_2$, participates in competing pathways leading respectively to nuclear or side chain chlorination.

EXPERIMENTAL

Typical Procedure.—An aqueous acetonitrile solution of sodium peroxodisulphate was bubbled with nitrogen for 0.75 h at room temperature. Near the end of the nitrogen purging the aromatic substrate was added. Known quantities of the remaining reagents were added at the end of the purging together with a magnetic stirrer. The flask was quickly stoppered, shaken, and placed in an oil-bath at a fixed temperature. With copper(II) chloride present the reaction mixture became green-yellow indicating formation of chlorocopper(II) complexes. After reaction had finished the flask was cooled and the contents extracted with ether.

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[25] R. Parsons, 'Handbook of Electrochemical Constants,' Butterworths, London, 1959, p. 73.

[26] See for example A. T. Thornton and G. S. Lawrence, *J.C.S. Dalton*, 1973, 1632.

[27] W. C. E. Higginson and M. E. Simpson, *J.C.S. Chem. Comm.*, 1974, 817.

[28] J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1968, **33**, 83.

[29] See for example N. Kornblum and F. W. Stuchal, *J. Amer. Chem. Soc.*, 1970, **92**, 1804; N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *ibid.*, 5513.

[30] G. A. Russell, R. K. Norris, and E. J. Panek, *J. Amer. Chem. Soc.*, 1971, **93**, 5839.

[31] R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1972, **94**, 683; *J. Org. Chem.*, 1972, **37**, 3570; 1973, **38**, 1407, 3020.

[32] D. Y. Myers, G. G. Stroegel, B. R. Ortiz de Montellano, and P. D. Gardner, *J. Amer. Chem. Soc.*, 1974, **96**, 1981.

[33] C. K. Mann and K. K. Barnes, 'Electrochemical Reactions in Non-aqueous Systems,' Dekker, New York, 1970.

[34] S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 1409.

[35] J. Bjerrum, *Kem. Maanedsbl. Nord. Handelsblad Kem. Ind.*, 1945, **26**, 24.

The ether extracts were washed, dried, and evaporated, and dry ether solutions of the product were made up for analysis by g.l.c. (Pye 104; Carbowax columns), and then subsequently by g.l.c.–mass spectrometry. Products were identified by mixed injections (g.l.c. analysis) and identical mass spectra with authentic materials. Quantitative analyses were carried out using the internal standard technique.

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