

Homolytic Halogen Replacement in Halogenobenzenes by Radiolytically Formed Aqueous Hydrogen (Tritium) Atoms

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Summary Replacement of halogen atoms by aqueous tritium atoms occurs in competition with hydrogen replacement, the relative importance of the two processes depending on the nature of the halogen and the concentration of added copper(II) ion

SELF-RADIOLYSIS of tritiated water produces aqueous hydrogen and tritium atoms. The organic substitution products formed by reaction of these tritium atoms with aromatic compounds in dilute solution (10^{-4} — 10^{-3} M) can be detected and assayed even at low irradiation intensities and minimal extent of chemical conversion¹. Relative rates for hydrogen replacement by tritium atoms have thus been measured for a range of aromatic compounds².

We now report that, in addition to this replacement of H by T, there occurs for some of the aromatic compounds examined, and most clearly for halogenobenzenes, the replacement of a substituent group by tritium ($\text{ArX} \rightarrow \text{ArT}$). The two reactions, H-replacement and X-replacement, are in mutual competition, and their relative rates were found by g.l.c. separation of the products, after addition of inactive carriers, and tritium assay (Table 1).

TABLE I

X-Replacement/H-replacement by tritium in aromatic compound

ArX	ArX	X-Replacement/ H-replacement
Mesitylene	<0.001
Toluene	<0.005
Anisole	0.03
t-Butylbenzene	0.05
Chlorobenzene	0.12
Bromobenzene	0.31
Iodobenzene	8.1

Both reactions are reduced in extent by addition of copper(II) sulphate in small concentration, but dehalogenation is affected considerably more than H-exchange. This is shown in Table 2 for bromobenzene, and a similar conclusion is reached for chlorobenzene. The addition of nickel(II) sulphate has a less pronounced effect on dehalogenation, which supports the view that hydrated electrons are not in the main responsible for this reaction.

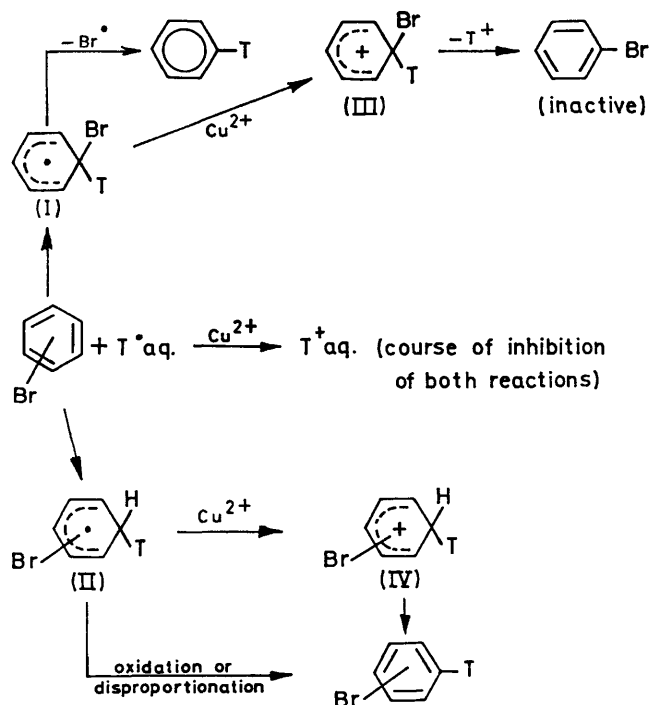
TABLE 2

Effect of copper(II) sulphate on product formation for bromobenzene

$10^4[\text{Cu}^{2+}]/\text{M}$	v_{PhT}^*	$v_{\text{C}_6\text{H}_4\text{TBr}}^\dagger$	X-Replacement/ H-replacement
0	137	435	0.31
25	50	274	0.18
50	29	232	0.13
75	18	190	0.09
100	12	187	0.06
200	7	141	0.05
350	5	91	0.05
500	3	71	0.04

* Rate of formation of PhT [units: (disintegrations/min) per day of reaction per dm^3 of solution per $(\text{Ci}/\text{dm}^3)^2$ of water activity]. † Rate of formation of $\text{C}_6\text{H}_4\text{TBr}$ in same units.

It is suggested that the following mechanism (see Scheme) accounts for the observations in all essentials. Both isotope exchange and dehalogenation are initiated by attack at different positions of the aromatic ring by hydrogen (tritium) atoms to give radicals (I) and (II). [The chlorine analogue of (I) is also known to be formed by attack of chlorine atoms on benzene.]³ Copper(II) ions are effective scavengers for hydrogen (and tritium) atoms and both reactions are therefore inhibited by copper(II) ions. Since copper(II) ions are known likewise to oxidise aliphatic radicals,⁴ they may also be expected to react with the substituted cyclohexadienyl radicals [(I), (II)] generated in the initiating steps. This oxidation gives rise to carbonium ions (cyclohexadienyl cations) (III) and (IV). (In a different context, the ready oxidation of phenylcyclohexadienyl radicals to cations has recently been put forward.⁵) Halogen loss from radical (I) (directly or by a radical-radical reaction) leads to labelled benzene and it is suggested that this is an important reaction in the absence of oxidising agents. On the other hand, the carbonium ion (III), formed by oxidation of (I), preferentially loses a proton (triton), rather than a bromine cation, in aqueous solution. This loss leads to the regeneration of inactive bromobenzene, *i.e.* there is a second reaction stage at which copper(II) ions



interfere with the dehalogenation reaction. The corresponding pathway for inhibition of the H-T exchange does not exist, since oxidation of radical (II) yields cation (IV) which, by virtue of the isotope effect discriminating against loss of tritium, will in the main give rise to labelled bromobenzene, the same product as in the absence of copper(II) ions. Hence H-replacement is less inhibited by copper(II) ions than Br-replacement.

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