FREE RADICAL SUBSTITUTION

1. a) Free radicals are atoms or groups of atoms which have a single unpaired electron.

   b) A photochemical reaction is a reaction which is brought about by light.

   c) A chain reaction is one in which for every reactive species you start off with, a new one is generated at the end, keeping the process going.

2. a) In the initiation stage, energy from UV light breaks the bond between the two chlorine atoms to produce two chlorine free radicals – each with an unpaired electron.

   In the first propagation reaction, a chlorine free radical hits a methane molecule and removes a hydrogen atom from it. This produces hydrogen chloride and a methyl radical.

   In the second propagation reaction the methyl radical hits a chlorine molecule, combines with one of the chlorine atoms, and in the process produces a new chlorine radical. The reaction is being propagated in the sense that this new chlorine radical can go through the same process again, generating yet another chlorine radical at the end – and so on.

   Termination happens when two free radicals combine without producing a new one. The equations show three possible ways this can happen. The chain is terminated because free radicals are being removed permanently from the reaction without generating any new ones.

   b) (i) $CH_3Cl + Cl\bullet \longrightarrow \bullet CH_2Cl + HCl$

   $\bullet CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl\bullet$

   (ii) $CH_2Cl_2 + Cl\bullet \longrightarrow \bullet CHCl_2 + HCl$

   $\bullet CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl\bullet$

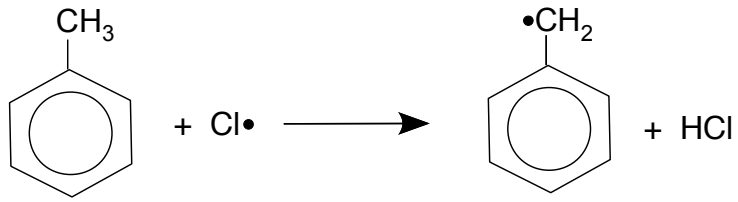
   (iii) $CHCl_3 + Cl\bullet \longrightarrow \bullet CCl_3 + HCl$

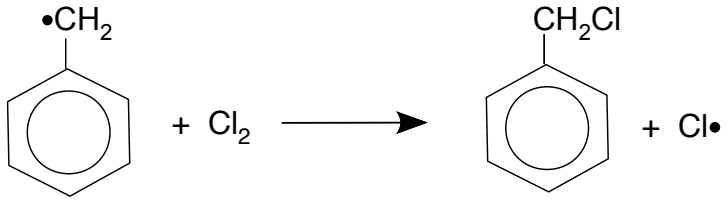
   $\bullet CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl\bullet$

3. a) $Cl_2 \xrightarrow{UV} 2Cl\bullet$

   The UV light provides the energy to break the bond between the two chlorine atoms.

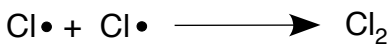
b)

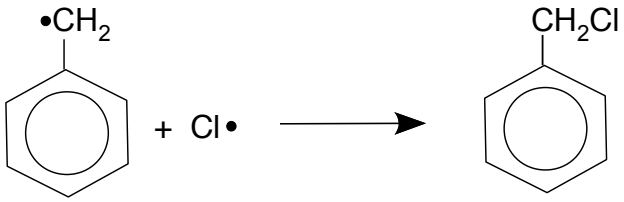




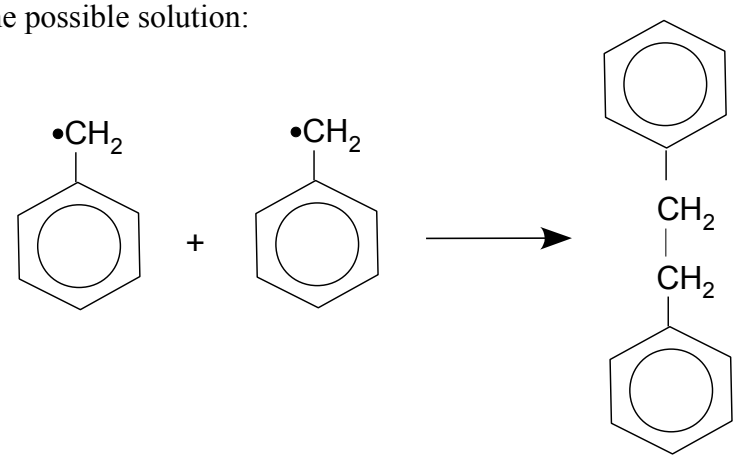
(Note: You may notice that I have drawn the dot for the unpaired electron in a slightly different place from the one on the Chemguide page. Technically, the unpaired electron is on the carbon as shown above, but it is probably more often drawn after the CH_2 group – as on the Chemguide page. It doesn't matter, and you must be familiar with either version.)

c) The two easy-to-draw ones are:





You could also have the one where two of the organic radicals join together, giving you two benzene rings joined by a $-CH_2-CH_2-$ bridge. There are various ways you could draw this. This is one possible solution:



(In fact you are more likely to draw this with the final molecule drawn horizontally rather than vertically, and the two radicals drawn with the two benzene rings rotated so that the CH_2 groups face each other. That is easy to do with a pencil and paper, but would have been a bit more bother with my drawing software. So you got this version!)