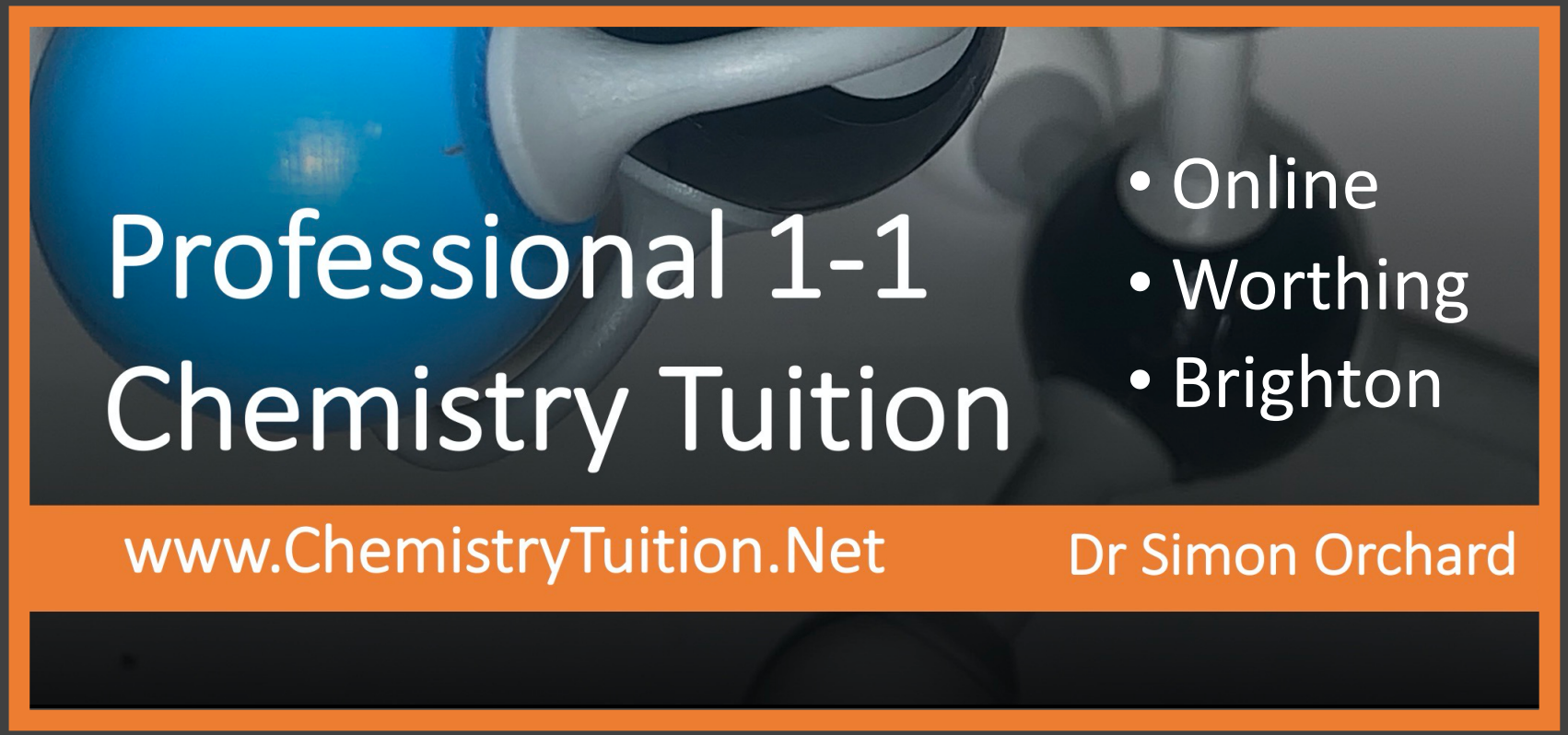
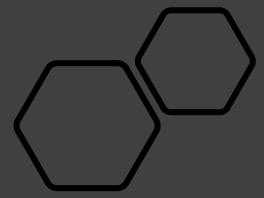


Halogenoalkanes



Naming Halogenoalkanes

CH_3Cl	chloromethane
CH_3CH_2I	iodoethane
$CH_3CH_2CH_2Br$	1-bromopropane
$CH_3CHBrCH_3$	2-bromopropane

Physical Properties

Liquids at room temperature

Immiscible with water as they do not form hydrogen bonds but they are miscible with alcohols.

Denser than water

For the same carbon chain the boiling point increases in the order of R-Cl < R-Br < R-I.

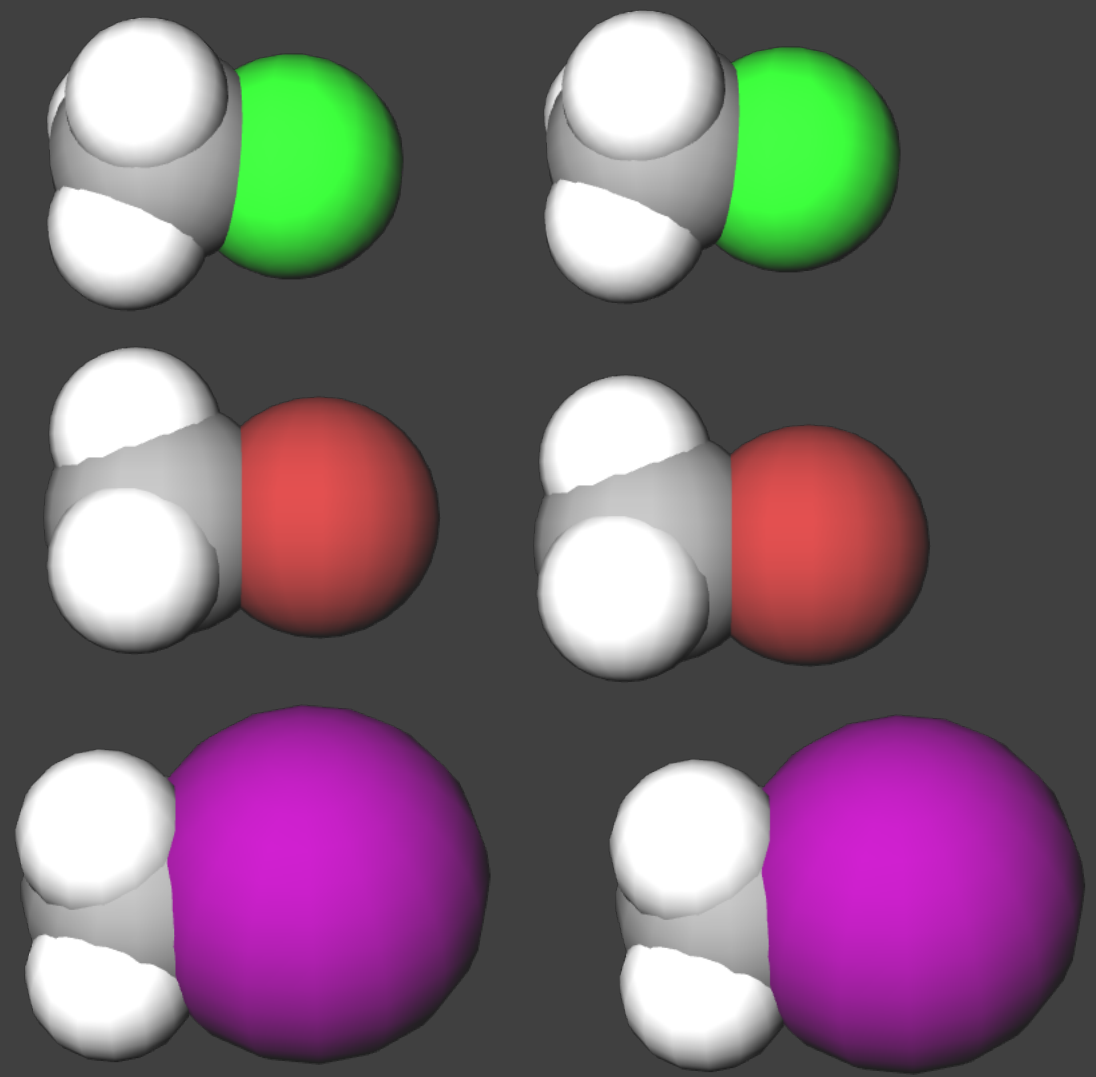
For the same carbon chain the boiling point increases down Group 7.

What intermolecular forces are in action?

Aren’t permanent dipole dipole stronger than London Forces

	Boiling Points
CH_3Cl	-24.2 °C
CH_3Br	3.56 °C
CH_3I	42 °C

Electron cloud filling model



Atomic Number
Electronegativity

17
Cl
Chlorine
3.16

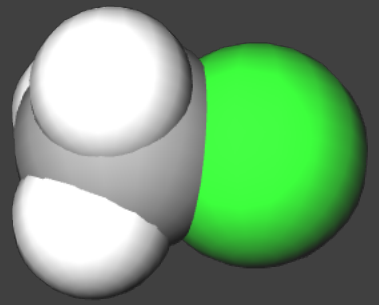
35
Br
Bromine
2.96

53
I
Iodine
2.66

Number of electrons
London Forces

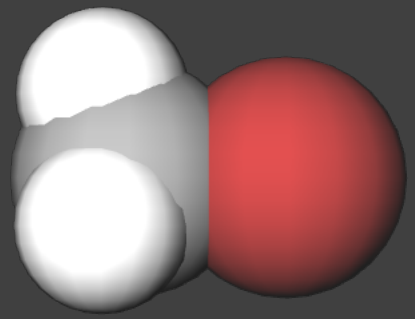
Electronegativity
Permanent
dipole - dipole

CH_3Cl



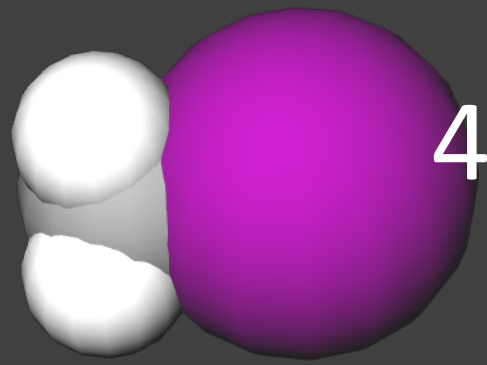
-24.2 °C

CH_3Br

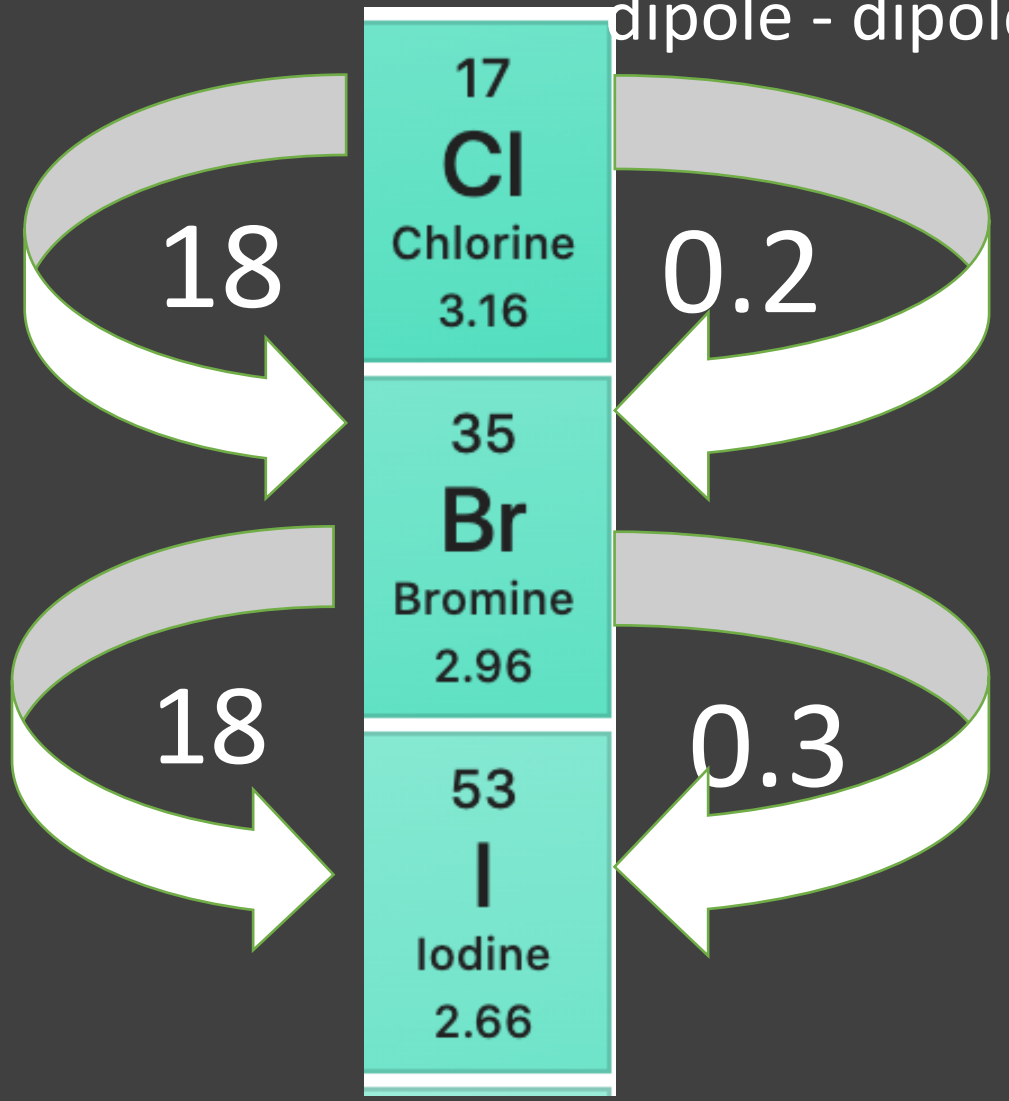


3.56 °C

CH_3I



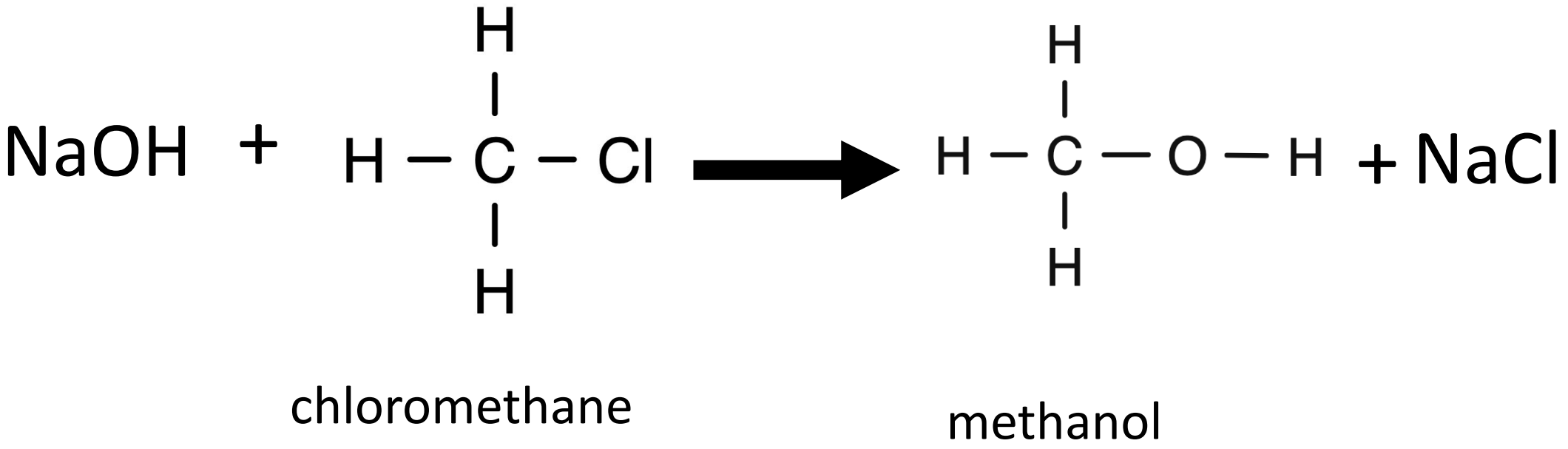
42 °C



Conclusion

London forces are more important than permanent dipole interactions between haloalkanes.

Reactions of halogenoalkanes



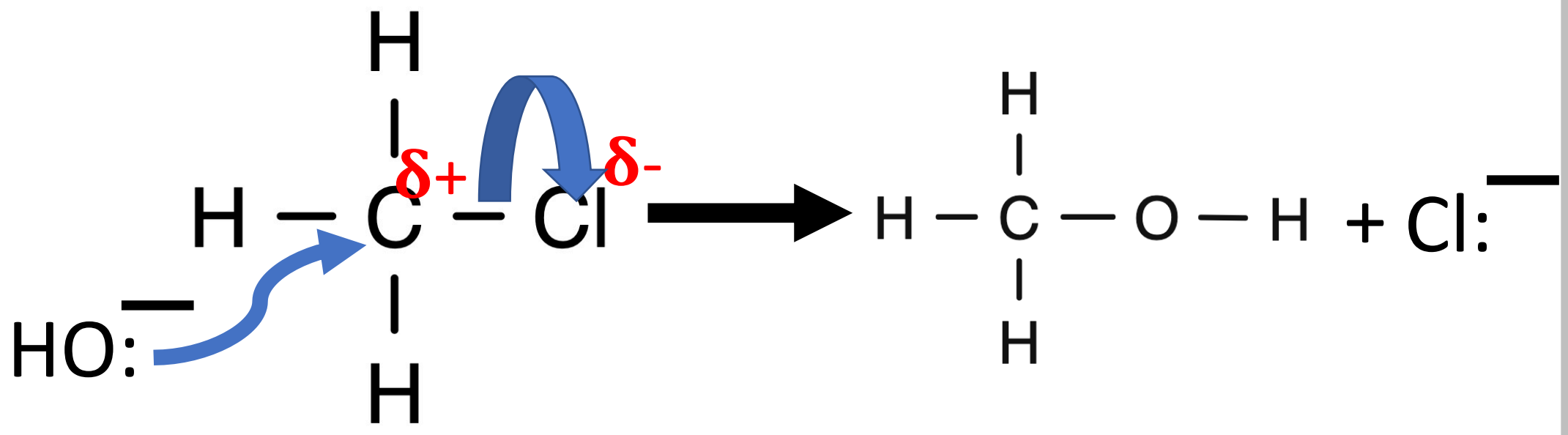
Mechanism

Substitution or addition?

What will be the attacking species from NaOH?

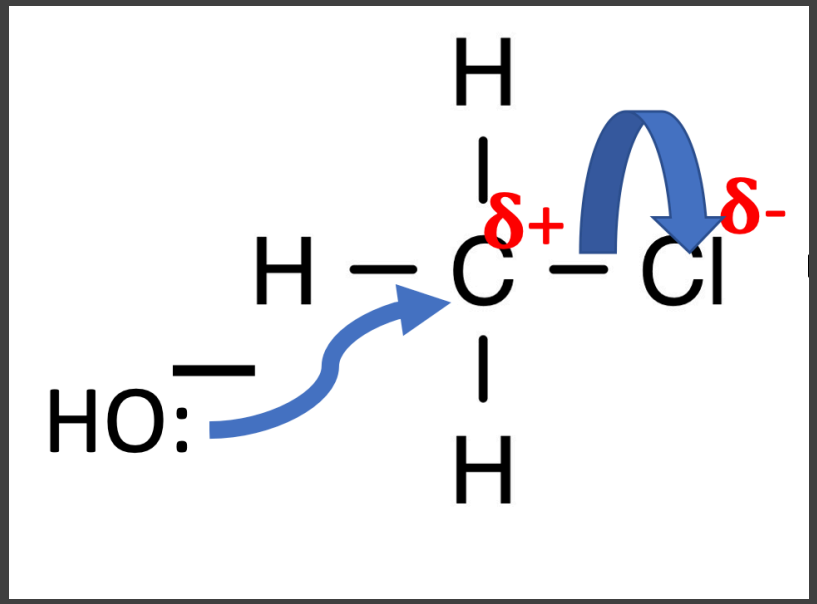
What do you know about the polarity of the C-Cl bond?

Mechanism: Nucleophilic Substitution

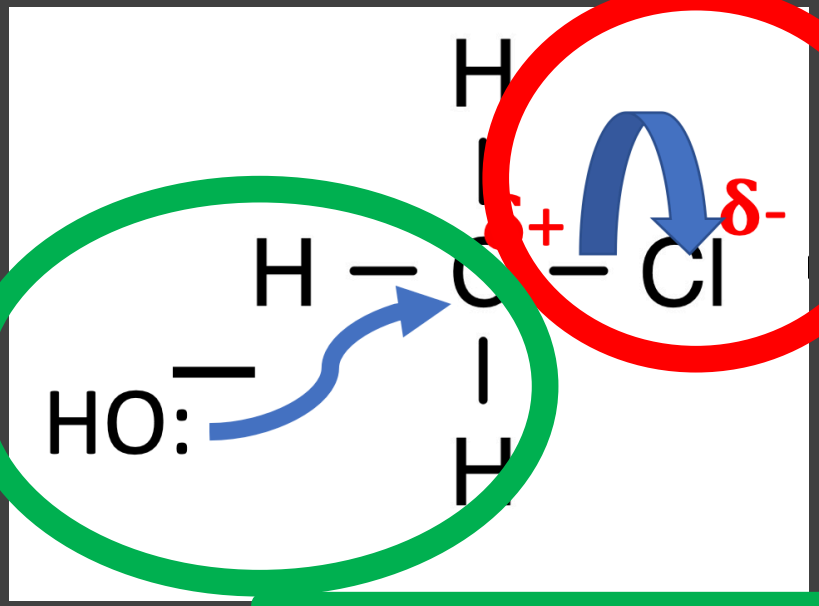


Rate of Nucleophilic Substitution

How will the rate of reaction change with the halogen? CH_3Cl vs CH_3Br vs CH_3I

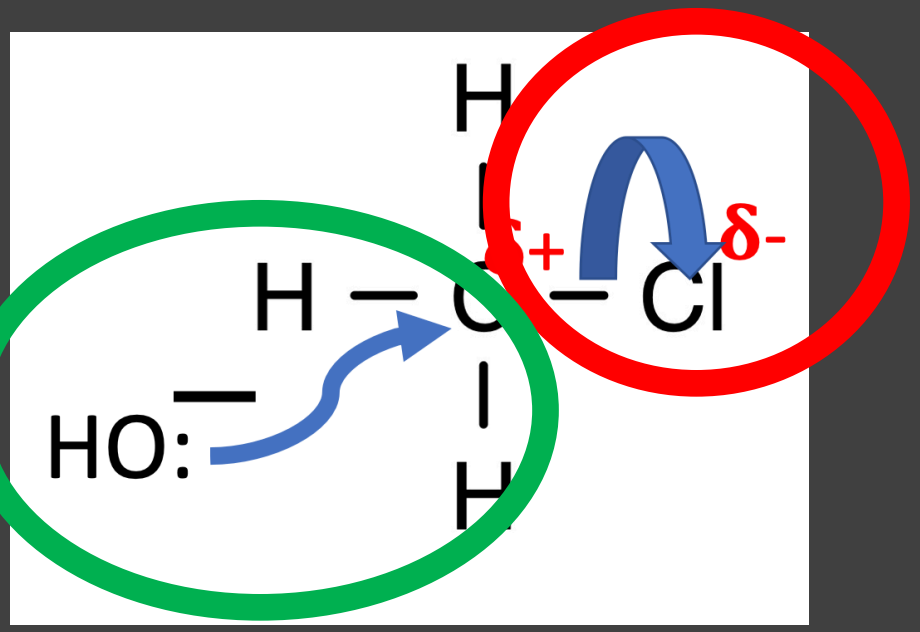


In this step
OH^- ion attacks the C atom and the C-X bond breaks



What property affects the rate of the C-Halogen bond breaking?

What property affects the rate at which the OH^- will attack the carbon atom?

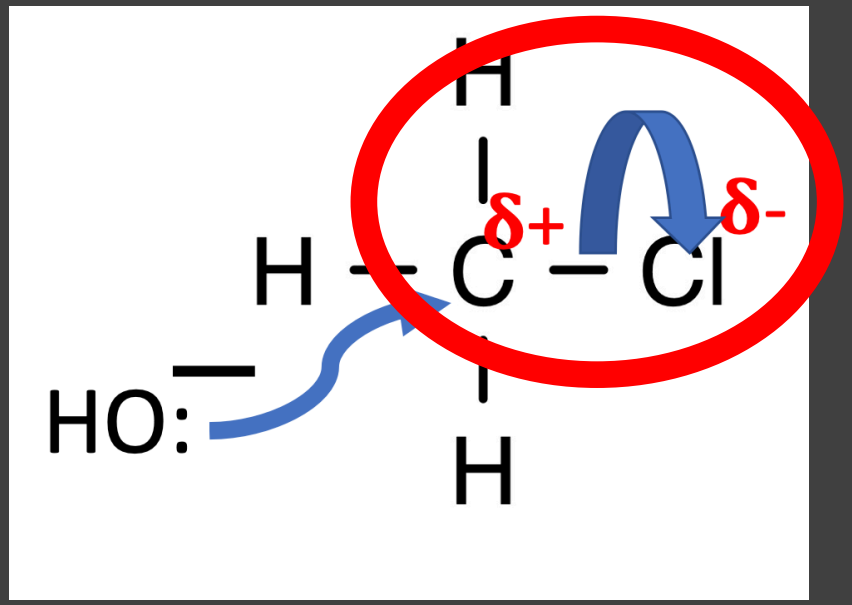


What property affects the rate of the C-Halogen bond breaking?

Carbon-Halogen Bond Enthalpy	
C-Cl	338 kJ/mol
C-Br	276 kJ/mol
C-I	238 kJ/mol

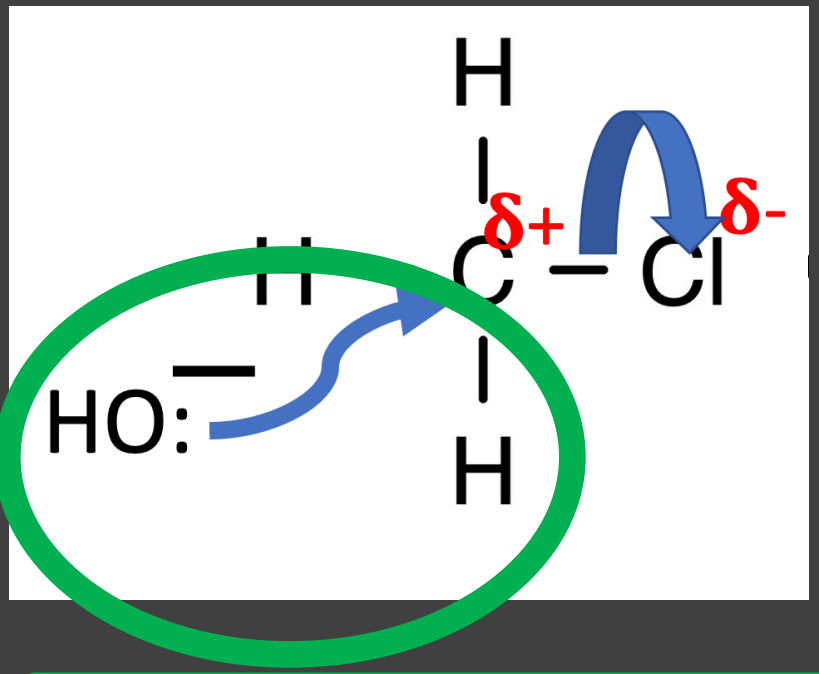
What property affects the rate at which the OH^- will attack the carbon atom?

Electronegativity Values	
Cl	3.16
Br	2.96
I	2.66



Carbon-Halogen Bond Enthalpy	
C-Cl	338 kJ/mol
C-Br	276 kJ/mol
C-I	238 kJ/mol

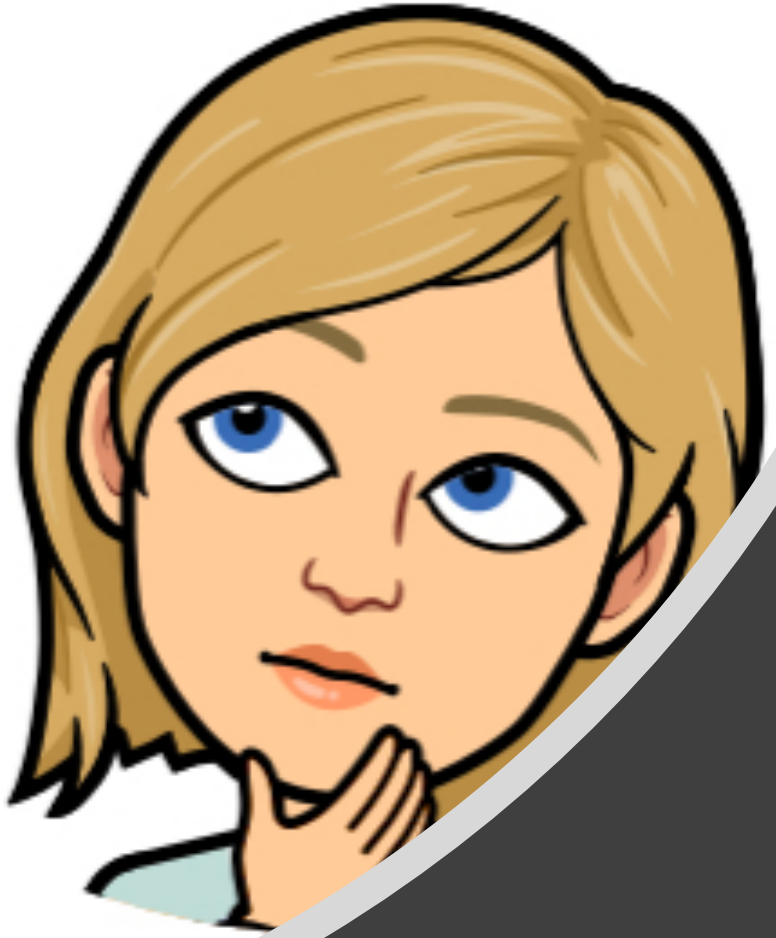
If the reaction rate increases as the C- Halogen bond enthalpy decreases, then breaking the C-X must be the most significant factor in determining how fast this step takes place.



If the reaction rate decreases as the C- Halogen bond polarity decreases, then the attack of the nucleophile must be the most significant factor in determining how fast this step takes place.

Electronegativity Values	
Cl	3.16
Br	2.96
I	2.66

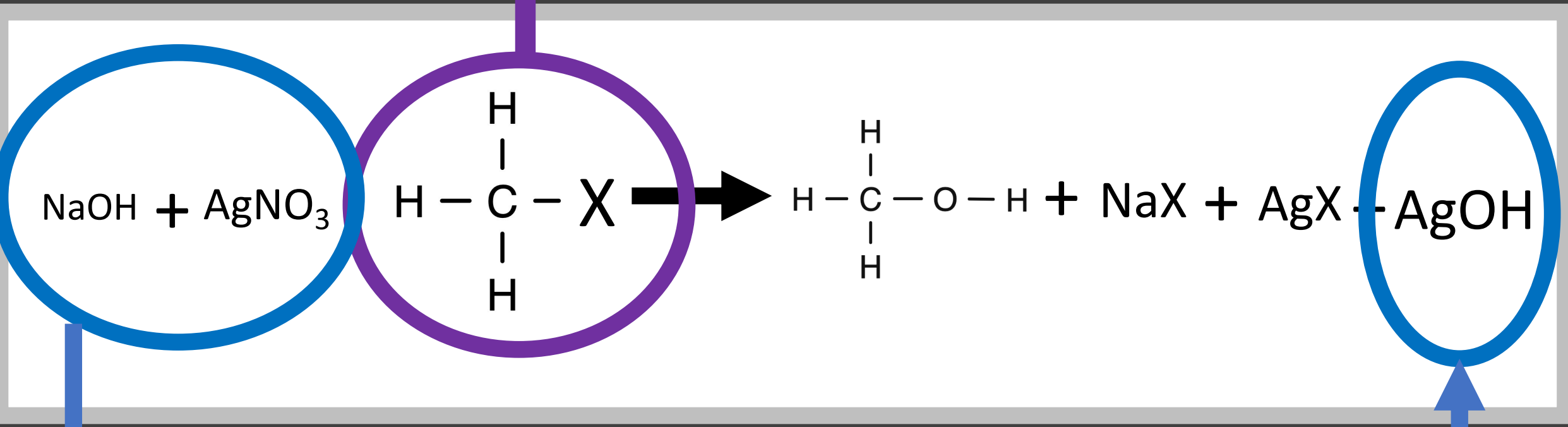
Investigating the Rate of Hydrolysis of Haloalkanes



How can we investigate this reaction experimentally?

We can time how long it takes for a precipitate of the silver halide to be produced if we add silver nitrate to the solution.

Halogenoalkanes and $AgNO_{3(aq)}$ will not mix



AgOH formed immediately

$Ag^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow AgOH_{(s)}$

Hints coming up..

Halogenoalkanes and $AgNO_{3(aq)}$ will not mix

→ Which solvent will hydrogen bond and mix with water **and** has a carbon chain?

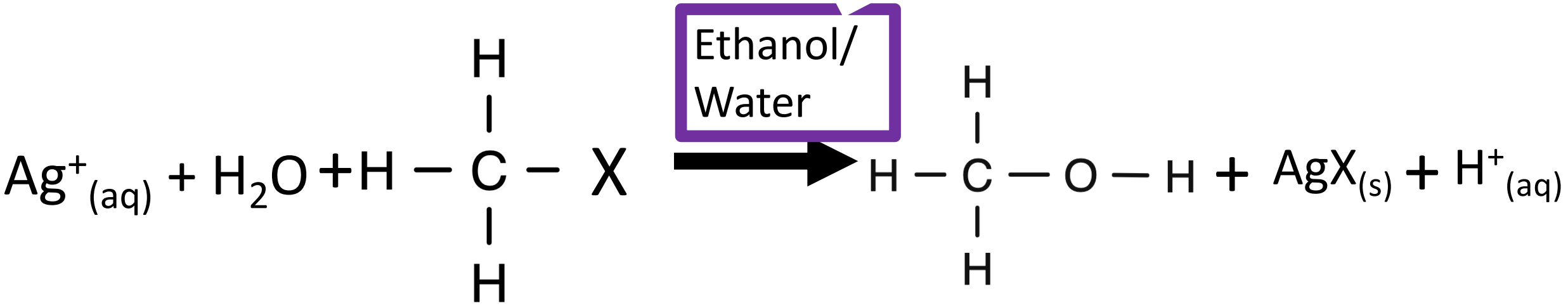
AgOH formed immediately

$Ag^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow AgOH_{(s)}$

→ The reaction will occur in water due to the OH^- ions being present but slowly

Experimental Details

Mix of H_2O/Ethanol allows the reactants to mix.



$$Ag^+_{(aq)} + H_2O + H-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-X \longrightarrow H-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-O-H + AgX_{(s)} + H^+_{(aq)}$$

Warm in using a water bath at 50°C

Heating at 50 °C in a water bath ensures constant temperature and reaction is fast enough

Time how long it takes for a precipitate of AgX to appear.

$$\text{Rate} \propto \frac{1}{\text{Time}}$$

The time for a precipitate of AgX to appear increases in the order:

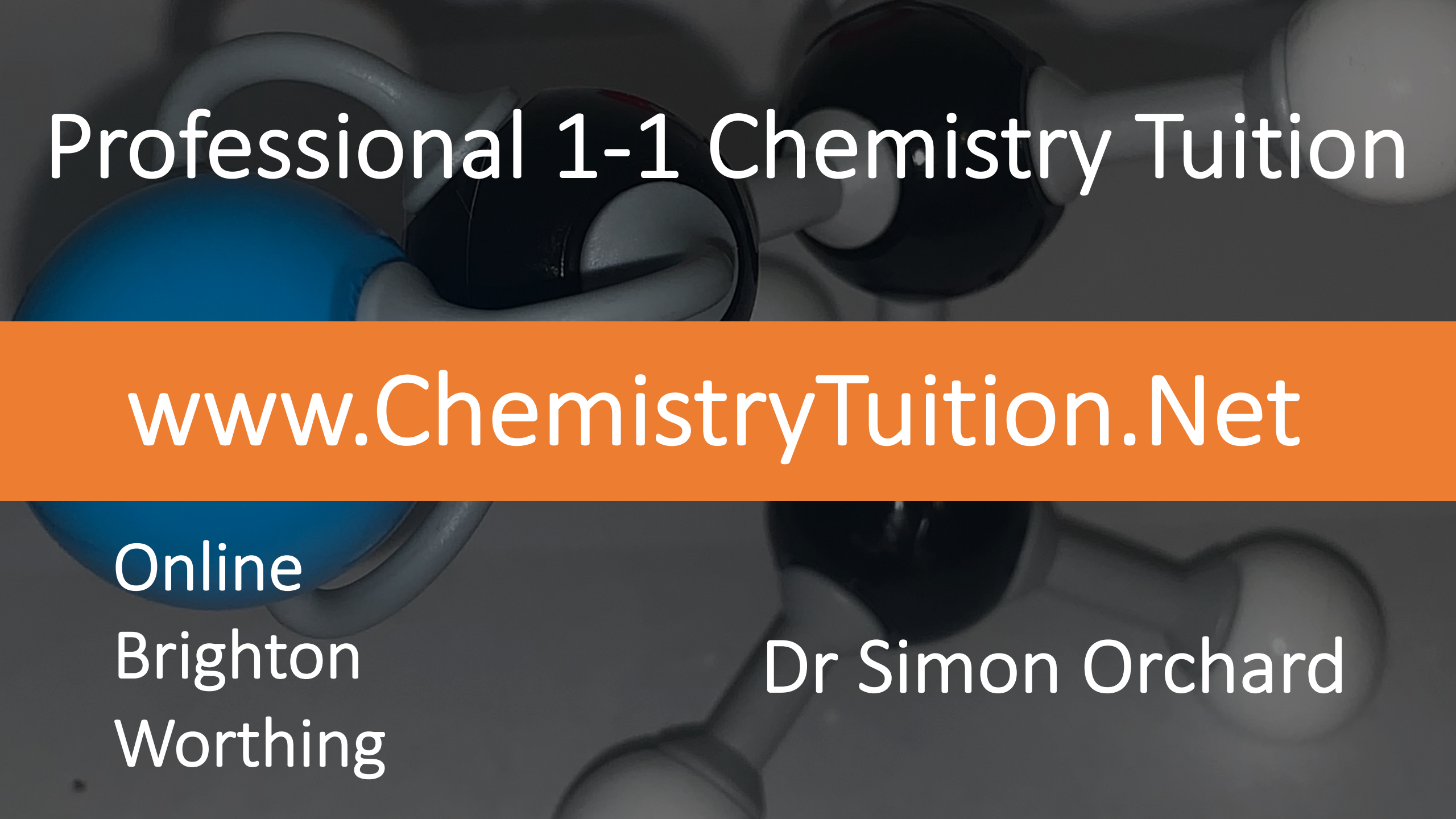
C-I Shortest time/Fastest Rate

C-Br

C-Cl Longest time/Slowest Rate

Therefore the strength of the C-X bond determines the rate of reaction.

As the halogen gets larger, the C-X bond gets longer and weaker and breaks more easily.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