Chem Factsheet

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Electronegativity – Predicting Reaction Products

This Factsheet gives guidance on the use of relative electronegativities to help you predict reactions involving reactants with polar covalent bonds. Before starting this Factsheet make sure you know the displayed formulas of organic functional groups.

1. Introduction

Electronegativity is a concept devised by Linus Pauling in 1932. He defined electronegativity as "the ability of an atom in a molecule to attract electrons to itself."

Similar definitions include "the power of an atom to withdraw electron density from a covalent bond" and "the ability of an atom to attract the bonding electrons in a covalent bond".

Either way, Pauling assigned a numerical value to each atom to indicate its relative electronegativity. As seen in the following table, these values vary up to 4.0 for fluorine,F.

Electronegativities of the s- and p-Block Elements for Periods 1 to 4

Group	1	2	3	4	5	6	7	0
Period 1	H 2.1							He
Period 2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Period 3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
Period 4	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0

Electronegativity Trends in the Periodic Table

(i) Periods

The electronegativity increases from left to right across a period.

- The nuclear charge increases across a period, causing the atomic radii to decrease.
- Within a period, the outer electrons are all in the same energy level, so shielding remains approximately constant.

Hence, the attraction of the nucleus of an atom for an electron pair in a covalent bond (i.e. its electronegativity) therefore **increases across a period** because the nuclear charge increases and the distance apart decreases.

This means that the covalent bond electron pair will be drawn closer to the nucleus of atoms **further to the right in the period**.

(ii) Groups

The electronegativity increases on moving up a group.

- On moving up a group, the atoms have smaller atomic radii, which means the outer electrons (bonding) are closer to the nucleus.
- On moving up a group, the atoms have fewer shells of electrons resulting in less shielding of the bonding electrons from the nuclear charge.

Hence, the attraction of the nucleus of an atom for an electron pair in a covalent bond (i.e. its electronegativity) therefore **increases up a group** because the distance apart and the shielding decrease (even though the nuclear charge decreases).

This means that the covalent bond electron pair will be drawn closer to the nucleus of atoms **nearer to the top of any group**.

Polar Covalent Bonds

In many organic molecules, carbon (electronegativity 2.5) atoms are often covalently bonded to more electronegative elements such as N, O, F, Cl and Br. These atoms will have a greater attraction than the C atom for the electrons in the covalent bond. Hence, the distribution of electron density in the bond becomes asymmetrical, resulting in a slightly positive (δ+ , electron-deficient) charge in the region of the C atom and a slightly negative (δ– , electron-rich) charge in the region of the atom bonded to C. The **covalent bond is said to be polar** and is represented as in the following examples:

$$\overset{\delta+}{C}\text{——}\overset{\delta-}{O} \quad \overset{\delta+}{C}\text{——}\overset{\delta-}{Cl} \quad \overset{\delta+}{C}\text{——}\overset{\delta-}{N} \quad \overset{\delta+}{C}\text{——}\overset{\delta-}{Br}$$

Electronegativity – Predicting Reaction Products

When a bimolecular reaction occurs that involves breaking polar covalent bonds in each molecule, the species with **opposite** partial charges combine to give the products.

The same prediction applies to reversible reactions. (A,B,C and D represent atoms or groups of atoms.)

i.e. $A^{\delta+}\text{—}B^{\delta-} + C^{\delta+}\text{—}D^{\delta-} \rightleftharpoons A^{\delta+}\text{—}D^{\delta-} + C^{\delta+}\text{—}B^{\delta-}$

The partial charges and the covalent bonds would not usually be included when writing the equation.

Thus the equation would be: $AB + CD \rightleftharpoons AD + CD$

When a chemical reaction occurs between a polar molecule and an ionic compound a similar idea applies:

i.e. $A^{\delta+}\text{—}B^{\delta-} + C^{+}D^{-} \rightarrow A^{\delta+}\text{—}D^{\delta-} + C^{+}B^{-}$

Note C^{+} is a spectator ion.

Hence, $A^{\delta+}\text{—}B^{\delta-} + D^{-} \rightarrow A^{\delta+}\text{—}D^{\delta-} + B^{-}$ is equally acceptable

1. Nucleophilic Substitution Reactions of Haloalkanes (Halogenoalkanes).

The carbon – halogen (X) covalent bond is polar, i.e. $C^{\delta+}\text{—}X^{\delta-}$. **Thus the $C^{\delta+}$ will attract an electron-rich nucleophile – a particle with an available lone pair.**

(a) Formation of Amines

Haloalkanes react with excess ammonia dissolved in ethanol ("ethanolic ammonia") when heated under pressure to initially produce **primary amines (C-NH$_2$)**. The polar bonds concerned are $C^{\delta+}Br^{\delta-}$ in the haloalkane and $N^{\delta-}H^{\delta+}$ in the ammonia. When these bonds break, the C bonds to N and H bonds to Br. It is easier to see what goes where if displayed formulae are used.

$$\mathbf{C^{\delta+}\text{—}Br^{\delta-} + N^{\delta-}\text{—}H^{\delta+} \rightarrow C^{\delta+}\text{—}N^{\delta-} + H^{\delta+}\text{—}Br^{\delta-}}$$

e.g. using bromomethane:

$$CH_3Br + NH_3 \rightarrow CH_3NH_2 + HBr$$

Note Since HBr is acidic and excess basic ammonia is present, salt formation will occur and a better equation would be:

$$CH_3Br + 2NH_3 \rightarrow CH_3NH_2 + NH_4Br$$

(b) Formation of Alcohols (Hydrolysis)

Haloalkanes are hydrolysed (or undergo nucleophilic substitution) by refluxing with aqueous alkali (e.g. NaOH or KOH). When the polar $C^{\delta+}$-$Br^{\delta-}$ breaks, the δ^- O of the OH^- nucleophile bonds to the carbon atom to form an **alcohol, (C-OH)**.

$$\mathbf{C^{\delta+}\text{—}Br^{\delta-} + {}^{-}O\text{—}H^{\delta+} \rightarrow C^{\delta+}\text{—}OH + Br^-}$$

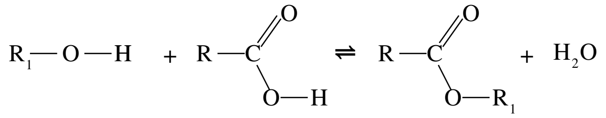
e.g. using bromoethane:

CH_3CH_2Br	+	^-OH	$\rightarrow$	CH_3CH_2OH	+	Br^-
molecule		nucleophile		molecule		nucleophile

Note: the spectator ion, Na^+, is left out.

2. Esterification and Hydrolysis of Esters

Alcohols, when warmed with a carboxylic acid in the presence of a strong acid catalyst (e.g. a few drops of conc. H_2SO_4), react to produce esters. Isotopic studies show that in most cases, the polar $O^{\delta-}$-$H^{\delta+}$ bond of the alcohol and the polar $C^{\delta+}$-$O^{\delta-}$ bond of the carboxylic acid both break. Hence, the C of the acid bonds to the O of the alcohol to produce the ester bond, and the O of the acid bonds to the H from the alcohol to give water.



$$O^{\delta-}\text{—}H^{\delta+} + C^{\delta+}\text{—}O^{\delta-} \rightarrow C^{\delta+}\text{—}O^{\delta-} + O^{\delta-}\text{—}H^{\delta+}$$

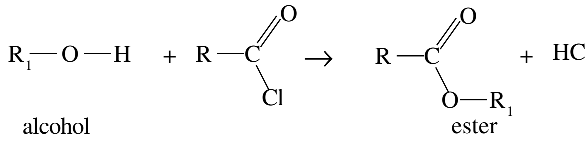
e.g. with methanol and ethanoic acid to form methyl ethanoate and water:

$$\mathbf{CH_3}OH + CH_3COOH \rightleftharpoons CH_3COO\mathbf{CH_3} + H_2O$$

The reverse reaction occurs when the ester is heated with a strong acid. The polar ester bond ($C^{\delta+}$-$O^{\delta-}$) breaks as does a polar $H^{\delta+}$-$O^{\delta-}$ in water. Opposite charges combine to reform the alcohol and carboxylic acid. Alkaline hydrolysis (e.g. NaOH) yields the salt of the carboxylic acid.

3. Addition-Elimination Reactions of Acyl Chlorides

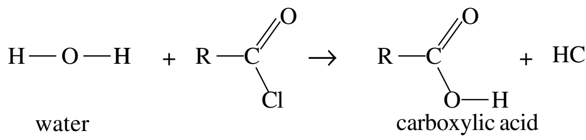
Water and alcohols have polar $O^{\delta-}$-$H^{\delta+}$ bonds. Acyl chlorides have polar $C^{\delta+}$-$Cl^{\delta-}$ bonds. Hydrogen chloride (seen as faint white fumes) is produced and the C of the acyl chloride and O of the alcohol or water also bond to give the organic product (ester or carboxylic acid).



$$O^{\delta-}\text{—}H^{\delta+} + C^{\delta+}\text{—}Cl^{\delta-} \rightarrow C^{\delta+}\text{—}O^{\delta-} + H^{\delta+}\text{—}Cl^{\delta-}$$

e.g. with methanol and ethanoyl choride to form methyl ethanoate and water:

$$\mathbf{CH_3}OH + CH_3COCl \rightarrow CH_3COO\mathbf{CH_3} + HCl$$

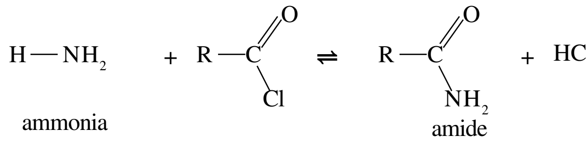


$$O^{\delta-}\text{—}H^{\delta+} + C^{\delta+}\text{—}Cl^{\delta-} \rightarrow C^{\delta+}\text{—}O^{\delta-} + H^{\delta+}\text{—}Cl^{\delta-}$$

e.g. with water and propanoyl choride to form propanoic acid:

$$\mathbf{H}_2O + CH_3CH_2CO\mathbf{Cl} \rightarrow CH_3CH_2COOH + \mathbf{HCl}$$

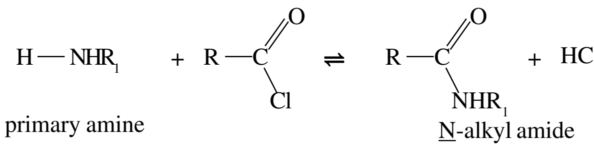
Ammonia and primary amines have polar $N^{\delta-}$-$H^{\delta+}$ bonds and so analogous reactions occur. This time amides or N-substituted amides result. However since HCl is acidic and NH_3 and RNH_2 are bases, salts are formed. Dense white smoke (NH_4Cl / RNH_3Cl) is seen. The acid-base reactions have not been included in the following equations – these equations will be acceptable in examinations when discussing the basis changes of the organic molecule.



$$N^{\delta-}\text{—}H^{\delta+} + C^{\delta+}\text{—}Cl^{\delta-} \rightarrow C^{\delta+}\text{—}N^{\delta-} + H^{\delta+}\text{—}Cl^{\delta-}$$

e.g. with ammonia and butanoyl choride to form butanamide:

$$\mathbf{NH_3} + CH_3CH_2CH_2CO\mathbf{Cl} \rightarrow CH_3CH_2CH_2CO\mathbf{NH_2} + \mathbf{HCl}$$

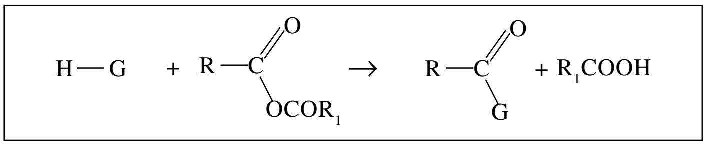


$$N^{\delta-}\text{—}H^{\delta+} + C^{\delta+}\text{—}Cl^{\delta-} \rightarrow C^{\delta+}\text{—}N^{\delta-} + H^{\delta+}\text{—}Cl^{\delta-}$$

e.g. with aminomethane (methylamine) and propanoyl choride to form N-methyl propanamide:

$$\mathbf{CH_3NH_2} + CH_3CH_2CO\mathbf{Cl} \rightarrow CH_3CH_2CO\mathbf{NHCH_3} + \mathbf{HCl}$$

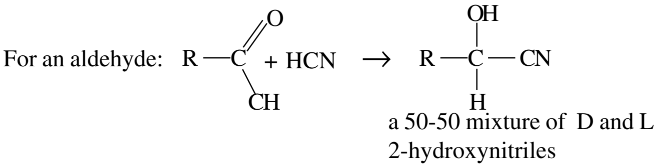
Acid anhydrides (R-CO)$_2$R) react in a similar way to acyl chlorides. The acid anhydride has a polar $C^{\delta+}$-$O^{\delta-}$ bond instead of a $C^{\delta+}$-$Cl^{\delta-}$ bond. Hence, a carboxylic acid is formed instead of hydrogen chloride.



Group G	H-G	RCOG Product
OH	Water, H_2O	Carboxylic acid, RCOOH
OR	Alcohol, ROH	Ester, RCOOR
NH_2	Ammonia, NH_3	Amide, $RCONH_2$
NHR	Amine, RNH_2	N-Alkyl amide, RCONHR

4. Nucleophilic Addition Reactions of Carbonyls with Hydrogen Cyanide.

Carbonyls have a polar $C^{\delta+}{=}O^{\delta-}$ bond and hydrogen cyanide a polar $H^{\delta+}\text{-}C^{\delta-}N$ bond. Hence the products have a new C-C bond and an O-H bond.



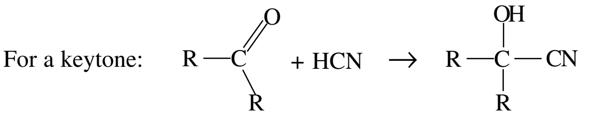
For an aldehyde:

a 50-50 mixture of D and L 2-hydroxynitriles

$$C^{\delta+}{=}O^{\delta-} + H^{\delta+}{-}C^{\delta-} \rightarrow HO{-}C{-}C$$

e.g. for propanal with HCN to form D- and L- 2-hydroxybutanenitrile

$$CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$$



For a keytone:

a 50-50 mixture of D and L 2-hydroxynitriles if R groups different

$$C^{\delta+}{=}O^{\delta-} + H^{\delta+}{-}C^{\delta-} \rightarrow HO{-}C{-}C$$

e.g. for propanone with HCN to form 2-hydroxy-2-methylpropanenitrile

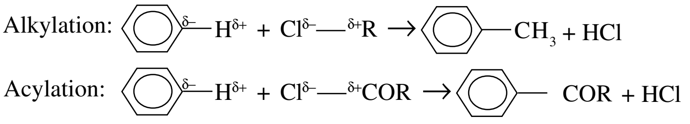
$$CH_3COCH_3 + HCN \rightarrow (CH_3)_2CH(OH)CN$$

Note: D and L isomers form for aldehydes and asymmetric ketones because they give a chiral centre (chiral C) where 4 different groups are attached. The mixture is 50:50 (racemic) because the carbonyl group of the aldehyde or ketone is planar, allowing equal opportunity for attack by the CN- nucleophile above or below that plane.

5. Friedel-Crafts Alkylation and Acylation Reactions (Electrophilic Substitution Reactions)

Alkyl chlorides and acyl chlorides have a polar $C^{\delta+}\text{-}Cl^{\delta-}$. The benzene ring has polar $C^{\delta-}\text{-}H^{\delta+}$. Hence, the product will contain a new C-C bond and HCl will be evolved. The catalyst is often the Lewis acid, anhydrous $AlCl_3$.

$$C^{\delta-}{-}H^{\delta+} + C^{\delta+}{-}Cl^{\delta-} \rightarrow C{-}C + H{-}Cl$$



e.g. Benzene with chloroethane to form ethylbenzene

$$C_6H_6 + CH_3CH_2Cl \rightarrow C_6H_5CH_2CH_3 + HCl$$

& benzene with ethanoyl chloride to form phenylethanone (methylphenyl ketone)

$$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$$

Many other less common reactions could also be predicted using this electronegativity difference principle. Just remember to "swap" the δ+'s and the δ-'s to give the products.

$$\mathbf{A^{\delta+}{-}B^{\delta-} + C^{\delta+}{-}D^{\delta-} \rightarrow A^{\delta+}{-}D^{\delta-} + C^{\delta+}{-}B^{\delta-}}$$

This does not predict reaction conditions or observations – you will have to learn them!

Questions

Use the differences in electronegativities to write equations for the reactions that occur when the following pairs of reactants are mixed. Draw out the reactant structures, decide the polarities and do the swap! Name the organic product(s).

1. Methanoic acid and ethanol
2. 2-iodobutane and excess ammonia
3. Methanoyl chloride and propan-1-ol
4. Benzene and 2-chloropropane
5. 1, 2-dibromoethane and sodium hydroxide
6. Propanoyl chloride and water
7. Ethanoyl chloride and ammonia
8. Methanal and hydrogen cyanide
9. Benzene and propanoyl chloride

Answers

1. $HCOOH + CH_3CH_2OH \rightarrow HCOOCH_2CH_3 + H_2O$
   Ethylmethanoate
2. $CH_3CH_2CHICH_3 + 2NH_3 \rightarrow CH_3CH_2CH(NH_2)CH_3 + NH_4I$
   2-aminobutane
3. $HCOCl + CH_3CH_2CH_2OH \rightarrow HCOOCH_2CH_2CH_3 + HCl$
   Propylmethanoate
4. $C_6H_6 + CH_3CH(Cl)CH_3 \rightarrow C_6H_5CH(CH_3)_2 + HCl$
   2-phenylpropane
5. $BrCH_2CH_2Br + 2OH^- \rightarrow HOCH_2CH_2OH + 2Br^-$
   Ethane-1,2-diol
6. $CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$
   Propanoic acid
7. $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$
   Ethanamide
8. $HCHO + HCN \rightarrow CH_2(OH)CN$
   2-hydroxyethanenitrile
9. $C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$
   1-phenylpropanone (ethylphenylkeytone)

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