Organic Chemistry I

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6. Properties and Reactions of Haloalkanes

PHYSICAL PROPERTIES OF HALOALKANES

The physical properties of the haloalkanes are quite distinct from those of the corresponding alkanes. The size of the halogen substituent and the polarity of the carbon-halogen bond affect bond strength, bond length, molecular polarity, and boiling point.

The bond strength of C–X decreases as the size of X increases

The C–X bond-dissociation energies in the halomethanes, CH_3X , decrease along the series F, CI, Br, I. At the same time, the C–X bond lengths increase.



A haloalkane

Table 6-1	C–X Leng Strer	C–X Bond Lengths and Bond Strengths in CH ₃ X				
Halo- methane	Bond length (Å)	Bond strength [kcal mol ⁻¹ (kJ mol ⁻¹)]				
CH ₃ F	1.385	110 H				
CH ₃ Cl	1.784	85 v (356) u el				
CH ₃ Br	1.929	d g 203 m				
CH ₃ I	2.139	57 57 (238) Decrease				

The bond between carbon and halogen is made up mainly by the overlapping of an sp^3 hybrid orbital on carbon with a *p* orbital on the halogen.

In the progression from fluorine to iodine in the periodic table, the size of the halogen increases, and the electron cloud around the halogen atom becomes more diffuse.

As a consequence of this growing mismatch in size between the halogen p orbital and the relatively compact orbital on carbon, bonding overlap diminishes along the series, leading to both longer and weaker C–X bonds.

This phenomenon is general: Short bonds are stronger than longer bonds.



The C–X bond is polarized

The electron density along the C–X bond is displaced in the direction of X, giving the halogen a partial negative charge (δ^-) and the carbon a partial positive charge (δ^+).

How does this bond polarization govern the chemical behavior of the haloalkanes?

The electrophilic δ^+ carbon atom is subject to attack by anions and other electron-rich, nucleophilic species. Cations and other electron-deficient species, however, attack the δ^- halogen.



Haloalkanes have higher boiling points than the corresponding alkanes

The polarity of the C–X bond affects the physical properties of the haloalkanes. Their boiling

points are generally higher than the coulombic attraction between the δ^+ (*dipole–dipole interaction*).

Boiling points also rise with increasi London forces arise from mutual corre



ding alkanes, largely because of < bond dipoles in the liquid state

It of greater London interactions. nong molecules.

This effect is strongest when the outer electrons are not held very tightly around the nucleus, as in the larger atoms.

Dipole–Dipole Attraction

$$\overset{\delta^+}{\overset{C}{\longrightarrow}} \overset{\delta^-}{\overset{X^-}{\longrightarrow}} \overset{\delta^+}{\overset{W^{*+}}{\longrightarrow}} \overset{\delta^+}{\overset{X^-}{\longrightarrow}} \overset{\delta^+}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\longrightarrow}} \overset{\delta^+}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\longrightarrow}} \overset{\delta^+}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\longrightarrow}} \overset{\delta^-}{\overset{X^+}{\to}} \overset{\delta^-}{\overset{$$

To measure it, we define the **polarizability** of an atom or group as the degree to which its electron cloud is deformed under the influence of an external electric field.

The more polarizable an atom or group, the stronger its London interactions, and the higher will be the boiling point.

Table 6-2	Boiling Points of Haloalkanes (R–X)									
		Boiling Point (°C)								
R	X =	Н	F	Cl	Br	Ι				
CH ₃		-161.7	-78.4	-24.2	3.6	42.4				
CH ₃ CH ₂		-88.6	-37.7	12.3	38.4	72.3				
CH ₃ (CH ₂) ₂	2	-42.1	-2.5	46.6	71.0	102.5				
CH ₃ (CH ₂) ₃	i -	-0.5	32.5	78.4	101.6	130.5				
CH ₃ (CH ₂) ₄		36.1	62.8	107.8	129.6	157.0				
CH ₃ (CH ₂) ₇	,	125.7	142.0	182.0	200.3	225.5				

Applications and Hazards of Haloalkanes: "Greener" Alternatives

Fully halogenated liquid bromomethanes: $CBrF_3$ and $CBrClF_2$ are extremely effective fire retardants. Heat-induced cleavage of the weak C–Br bond releases bromine atoms, which suppress combustion by inhibiting the free-radical chain reactions occurring in flames.

Like Freon refrigerants, bromoalkanes are ozone depleting and have been banned for all uses except fire-suppression systems in aircraft engines.

Phosphorus tribromide, PBr₃, a non-ozone-depleting liquid with a high weight percent of bromine, is a promising replacement.

The polarity of the carbon–halogen bond makes haloalkanes useful for applications such as dry cleaning of clothing and degreasing of mechanical and electronic components.

This solvent is safe, stable, usable for a wide variety of industrial functions, and may be readily recovered and recycled.

NUCLEOPHILIC SUBSTITUTION

Haloalkanes contain an electrophilic carbon atom, which may react with nucleophiles substances that contain an unshared electron pair.

The nucleophile can be an anion, such as hydroxide (-:OH), or a neutral species, such as ammonia (:NH₃).

A great many species are transformed in this way, particularly in solution.

Nucleophiles attack electrophilic centers



In the first example, a negatively charged nucleophile reacts with a haloalkane to yield a neutral substitution product.

In the second example, an uncharged Nu produces a positively charged product, which, together with the counterion, constitutes a salt.

In both cases, the group displaced is the halide ion, X⁻, which is called the **leaving group**.

The general term **substrate** (*substratus,* Latin, to have been subjected) is applied to the organic starting material—e.g., the haloalkane—that is the target of attack by a nucleophile.

Nucleophilic substitution changes the functional group in a molecule.

Methyl and primary haloalkanes give the "cleanest" substitutions, relatively free of side products.

Table 6-3	The Diversity of Nucleoph	nilic Subs ¹	titution				
Reaction number	Substrate		Nucleophile		Product		Leaving group
1.	CH ₃ Cl: Chloromethane	+	нö:-	\longrightarrow	CH ₃ OH Methanol	+	:Cl:-
2.	CH ₃ CH ₂ I: Iodoethane	+	CH ₃ Ö:-	\longrightarrow	CH ₃ CH ₂ OCH ₃ Methoxyethane	+	:ï:-
3.	H $CH_{3}CCH_{2}CH_{3}$ $Br:$	+	:Ï:-	\longrightarrow	H CH ₃ CCH ₂ CH ₃ :I:	+	: <u>B</u> r:-
	2-Bromobutane				2-Iodobutane		
4.	H CH ₃ CCH ₂ L: CH ₃ 1-Iodo-2-methylpropane	+	:N≡C:⁻	\rightarrow	H $CH_3CCH_2C \equiv N:$ CH_3 CH_3 $3-Methylbutanenitrile$	+	:ï:-
5.	Bromocyclohexane	+	CH₃S:-	\longrightarrow	SCH ₃ Methylthiocyclohexane	+	:₿r:⁻
6.	CH ₃ CH ₂ I: Indoethane	+	:NH ₃	\longrightarrow	$CH_3CH_2NH_3$ Ethylammonium iodide	+	:ï:-
7.	CH ₃ Br: Bromomethane	+	: P(CH ₃) ₃	\longrightarrow	CH ₃ CH ₃ PCH ₃ CH ₃ CH ₃ Tetramethylphosphonium	+	:Br:-

bromide

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REACTION MECHANISMS INVOLVING POLAR FUNCTIONAL GROUPS: USING "ELECTRON-PUSHING" ARROWS

Nucleophilic substitution is an example of a polar reaction: It includes charged species and polarized bonds.

Opposite charges attract—nucleophiles are attracted to electrophiles—by *moving electrons* from electron-rich to electron-poor sites.

Acid-base processes require electron movement. The Brønsted-Lowry process in which the acid HCI donates a proton to a molecule of water in aqueous solution:



Curved-Arrow Representations of Several Common Types of Mechanisms



THE NUCLEOPHILIC SUBSTITUTION MECHANISM: KINETICS

When a mixture of chloromethane and sodium hydroxide in water is heated, a high yield of two compounds—methanol and sodium chloride—is the result.

Rate equation or **rate law**: rate of product formation with several different concentrations of the starting materials. $CH_3Cl + NaOH$

$\int_{H_2O, \Delta} H_2O, \Delta$ $CH_3OH + NaC1$

"Δ" means that the reaction mixture is heated.

The reaction of chloromethane with sodium hydroxide is bimolecular

Measuring either the disappearance of one of the reactants or the appearance of one of the products.

In the reaction of chloromethane with sodium hydroxide, the rate depends on the initial concentrations of *both* of the reagents, a *second-order* process:

 $Rate = k[CH_3Cl][HO^-] mol L^{-1} s^{-1}$

Bimolecular nucleophilic substitution, abbreviated as $S_N 2$ (S stands for substitution, N for nucleophilic, and 2 for bimolecular) is a concerted, one-step process

The nucleophile attacks the haloalkane, with simultaneous expulsion of the leaving group. Bond making takes place *at the same time* as bond breaking (a **concerted** reaction).



2. Backside displacement, The nucleophile approaches carbon from the side opposite the leaving group.



Note that the formation of the transition state is *not* a separate step; the transition state only describes the geometric arrangement of the reacting species as they pass through the *maximum energy point* of a *single-step* process.