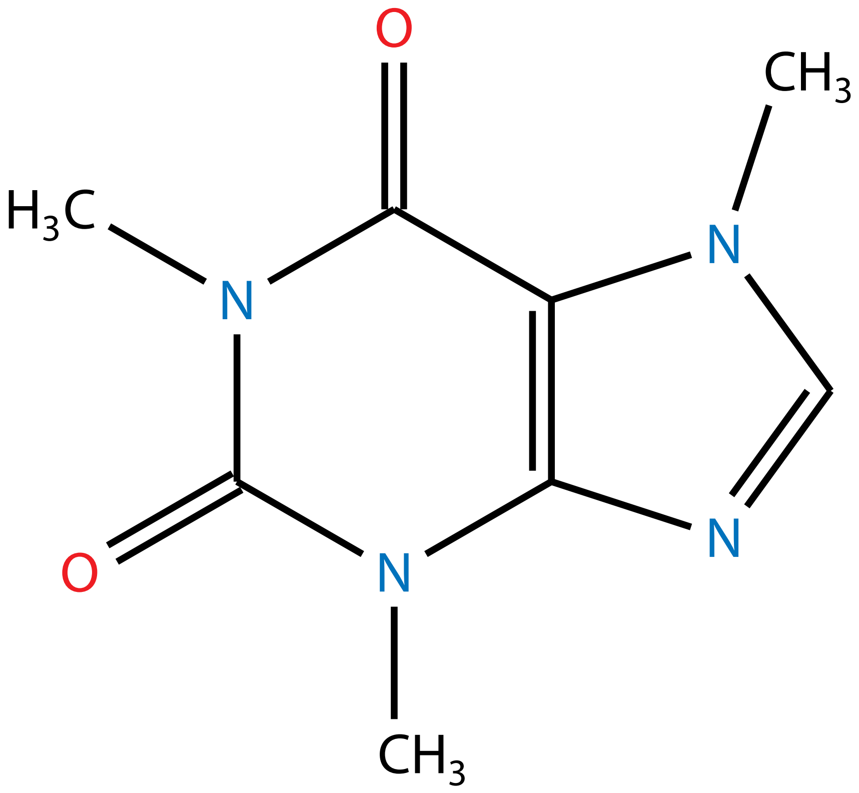
Organic Chemistry


O
CH3
H3C
N
N
N
O
N
CH3

$C_8H_{10}N_4O_2$

1,3,7-trimethylpurine-2,6-dione

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git: `e4ff492f05ab7c31e6278dbe0845570d7f46e7f2`

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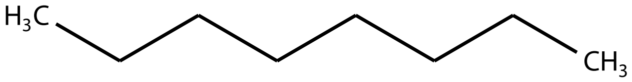
PART I

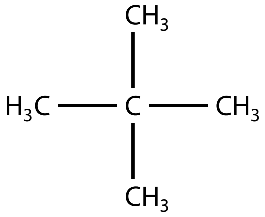
Alkanes

1 Open Chain

Open chain alkanes have the general formula of C_nH_{2n+2}. They are called 'open-chain' because the two ends of the chain are separate, in contrast with cycloalkanes. Open chain alkanes can either be straight or branch; the terminology should be pretty much self explanatory.



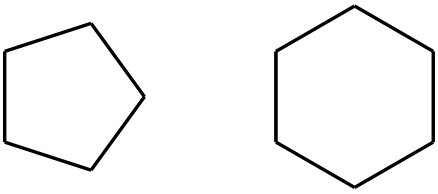
Octane is an example of a straight-chain alkane.]



2,2-dimethylpropane is an example of a branched alkane.

2 Cycloalkanes

Cycloalkanes are alkanes where the carbon atoms at either end of the chain are bonded together, forming a closed loop and taking the shape of regular polygons. They have the general formula C_nH_{2n}



Cyclopentane (left) and cyclohexane (right)

3 Physical Properties

3.1 Melting and Boiling Points

The melting and boiling points of alkanes follow a simple pattern. Due to the fact that they rely solely on induced dipole interactions for intermolecular bonding, both melting and boiling points increase with the length of the carbon chain, and by extension M_r.

However, because branched alkanes have a smaller surface area for a given number of carbon atoms than straight-chained alkanes, their melting and boiling points will be lower, due to a smaller area for polarisation.

3.2 Density

Most liquid alkanes, up to a certain point, are less dense than water. Additionally, since they are insoluble, they form an immiscible layer above water.

As the number of carbon atoms increases, the strength of the intermolecular interactions will increase as well — this forces each molecule ever so slightly closer together, marginally increasing density.

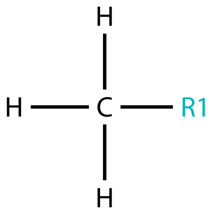
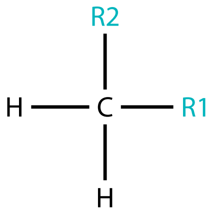
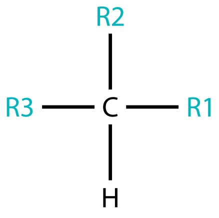
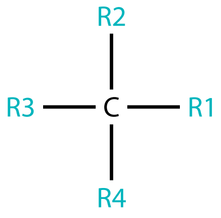
3.3 Solubility

As described before, alkanes rely only on induced-dipole interactions for intermolecular bonding; they are insoluble in polar solvents such as water. However, they are highly soluble in non-polar solvents like CCl_4. In fact, since solubility is dependent on the strength of solvent-solute bonds, larger alkanes will be more soluble in non-polar solvents.

4 Classification of Carbons

This applies to many things — carbons, halogenoalkanes, and alcohols. Essentially, the classification of an atom with substituent groups refers to the number of such groups attached to the carbon, and the number of hydrogens (ie. unfilled slots so to speak) attached to it.

As example, there are 4 possible classifications of carbons in an alkane: *primary*, *secondary*, *tertiary*, and *quaternary*.

Primary (1°)	Secondary (2°)	Tertiary (3°)	Quaternary (4°)
			

5 Alkane Reactions

5.1 Free Radical Substitution

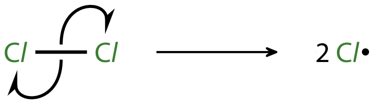
5.1.1 Mechanism of Reaction

In the steps below, the free radical substitution of methane (CH_4) by chlorine (Cl_2) will be used. This applies for any alkane, and a sufficiently reactive halogen.

Conditions: UV Light, Br_2 / Cl_2 gas
Observations: ***Reddish-brown*** Br_2 / *yellowish-green* Cl_2 decolourises.

Stage I. *Initiation*

The $Cl{-}Cl$ bond is *homolytically* broken to form 2 Cl radicals. The energy required to break this bond is provided by the UV light.



Stage II. *Propagation*

The highly reactive Cl radicals then react with the CH_4 molecules, bonding with one of the hydrogen atoms to form HCl and a carbocation radical, CH_3.

$$Cl\bullet + CH_4 \longrightarrow \bullet CH_3 + HCl$$

$$Cl_2 + \bullet CH_3 \longrightarrow CH_3Cl + Cl\bullet$$

This newly-minted CH_3 radical can react with a Cl_2 molecule to form CH_3Cl and another Cl radical, thus recreating the consumed radical. As long as the supply of Cl_2 gas has not been exhausted, this reaction can continue, and no additional UV light is required to sustain it.

Stage III. *Termination*

In the termination stage, two radicals combine to form stable products, effectively terminating the chain reaction.

$$\begin{aligned} Cl\bullet &+ Cl\bullet \longrightarrow Cl_2 \\ \bullet CH_3 &+ \bullet CH_3 \longrightarrow CH_3CH_3 \\ Cl\bullet &+ \bullet CH_3 \longrightarrow CH_3Cl \end{aligned}$$

Once all the radicals have been consumed in this manner, the reaction will stop, unless more UV light is provided (along with more Cl_2 gas).

5.1.2 Multi-substitution

Free radical substitution of alkanes is usually not the preferred way to produce halogenated alkanes, due to the random nature of the process and the possibility of multi-substitution, where more than one halogen atom has been substituted onto the alkane.

If there are still Cl radicals remaining in the reaction chamber, CH_3Cl formed during the termination stage can still react, forming a CH_2Cl radical, which can continue to react.

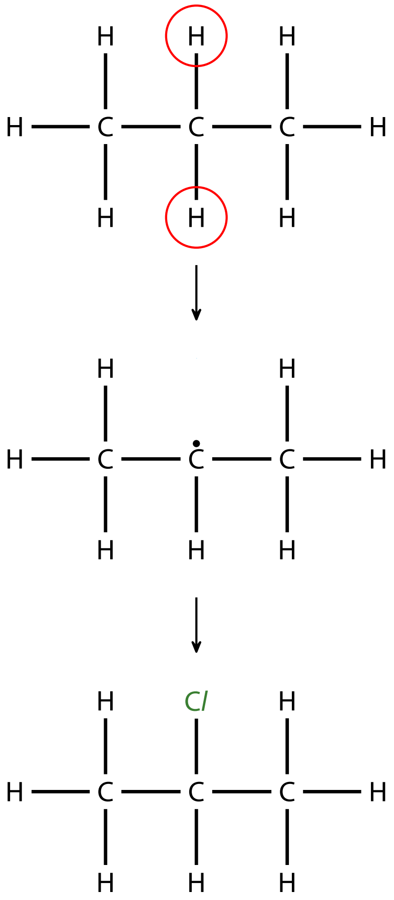
$$\begin{aligned} CH_3Cl &+ Cl\bullet \longrightarrow \bullet CH_2Cl \\ CH_2Cl\bullet &+ Cl_2 \longrightarrow CH_2Cl_2\bullet + Cl\bullet \end{aligned}$$

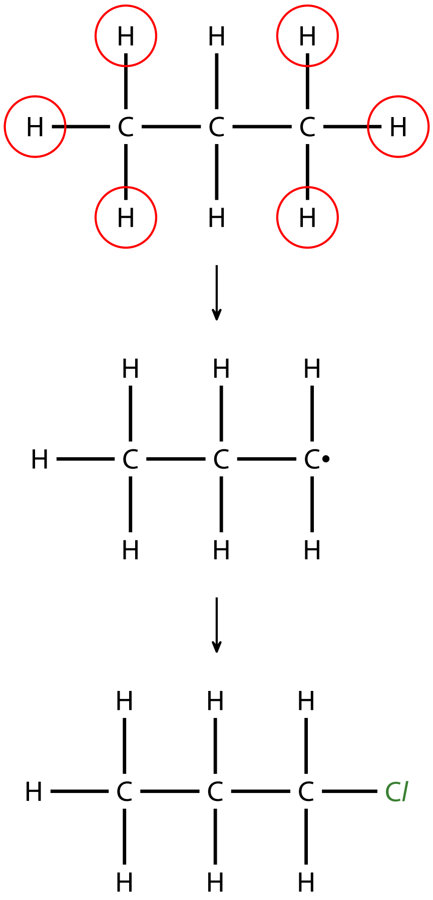
Indeed, this can continue *ad-infinitum*, until all the hydrogen atoms on the alkane have been substituted. In the case of methane, this results in the formation of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

In fact, there will also be a small amount of alkanes with more than 1 carbon in the chain; this is due to the possibility of two molecules of $\bullet CH_2Cl$ reacting, which then has its hydrogens further substituted.

5.1.3 Isomerism of Products

Because every hydrogen atom can be substituted by a halogen atom, alkanes with 3 or more carbon atoms in the chain can form isomers. The probability of the formation of each isomer depends on both the number of possible hydrogen atoms that can be substituted to result in it, as well as the stability of the carbon radical intermediate.





In the example above, propane can be substituted by Cl to form 2 different isomers, 2- chloropropane and 1-chloropropane. Only 2 hydrogens can be substituted to form the former, while 6 hydrogens can be substituted to form the latter. Thus, the *expected* ratio of products from the free radical substitution of propane with chlorine is 2 : 6 in favour of 1-chloromethane.

However, the stability of the carbon radical intermediate also plays a part in the ratio of products. For 1-chloropropane, it involves forming a carbon radical on carbon 1, which only has 1 electron-donating alkyl group (through the induction effect) to stabilise the positive charge.

On the other hand, for 2-chloropropane, the positive charge is on carbon 2, which has 2 electron-donating alkyl groups to stabilise it. Thus, the intermediate is more stable, and hence 2-chloropropane is more likely to form. Therefore, the actual ratio of products is around 4 : 6, not 2 : 6.

5.1.4 Halogen Reactivity

The reactivity of the free radical substitution naturally depends on the species of halogen that is reacting. As is typical of halogens, the reactivity increases in this order: $I_2 < Br_2 < Cl_2 < F_2$. In fact, the substitution by fluorine is too reactive — even in the dark and at room temperature. On the other hand, the substitution of iodine is not feasible ($\Delta G > 0$).

In the propagation steps of the reaction, several bonds are formed and broken. Using X as a halogen atom:

$\Delta H_1 = \mathrm{BE(C{-}H)} - \mathrm{BE(H{-}X)}$ $\qquad CH_3{-}H + X\bullet \longrightarrow \bullet CH_3 + H{-}X$
$\Delta H_2 = \mathrm{BE(X{-}X)} - \mathrm{BE(C{-}X)}$ $\qquad \bullet CH_3 + X{-}X \longrightarrow CH_3{-}X + X\bullet$
$\Delta H_r = \Delta H_1 + \Delta H_2$ $\qquad CH_4 + X_2 \longrightarrow CH_3X + HX$

The values of the bond energies for H–X, X–X, and C–X are below:

	$H{-}X$ / kJ mol^{-1}	$H{-}X$ / kJ mol^{-1}	$H{-}X$ / kJ mol^{-1}	ΔH_r / kJ mol^{-1}
F_2	562	484	158	−478
Cl_2	431	340	244	−117
Br_2	366	280	193	−43
I_2	299	240	151	+22

As can be seen, the reaction with F_2 is highly exothermic; the F–F bond energy is relatively small, hence the reaction is highly spontaneous — even at room temperature and without UV light, since the initiation stage requires little energy to progress.

On the other hand the ΔH of the reaction with I_2 is positive, hence the reaction is not as spontaneous, and the rate of reaction is very slow.

5.2 Combustion

Alkanes are a type of combustible fuel, and there exists a general formula describing the required amounts of O_2 to combust a given hydrocarbon.

$$C_xH_y \quad + \quad (x + \tfrac{y}{4})\, O_2 \quad \longrightarrow \quad x\, CO_2 \quad + \quad \tfrac{y}{2}\, H_2O$$

Note that while this combustion process is highly exothermic, it still has a high activation energy, and requires an energy input like a spark to begin the reaction.