

ORGANIC CHEMISTRY 1 LECTURE GUIDE 2019

BY RHETT C. SMITH

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By Rhett C. Smith, Ph.D.

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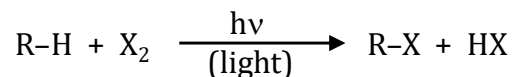
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Organic Chemistry 1 Primer 2019,

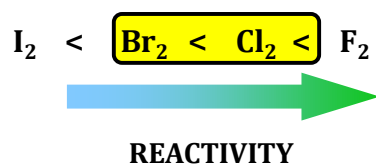
by Rhett C. Smith, Andrew G. Tennyson, and Tania Houjeiry

Lecture Topic III.18: Radicals II
Radical Halogenation of Alkanes

Alkyl halides can also be prepared from alkanes. Alkanes do not have very polar bonds, and do not readily react with common acids or bases. If we generate a very reactive species, like a **radical** we can observe reactions of alkanes. A good way to generate a halide radical is by excitation of X_2 with light.



The dihalides have different reactivities towards radical formation, so only **Cl₂** and **Br₂** are commonly used in the above reaction:



Because we are using such reactive species (radicals) it is often difficult to control these reaction to yield a single product, as we will see ...

Notes

Lecture Topic III.18: Radicals II
Radical Halogenation of Alkanes

We can write the discrete steps of the **radical chain mechanism**:

(A) Initiation

(B) Propagation

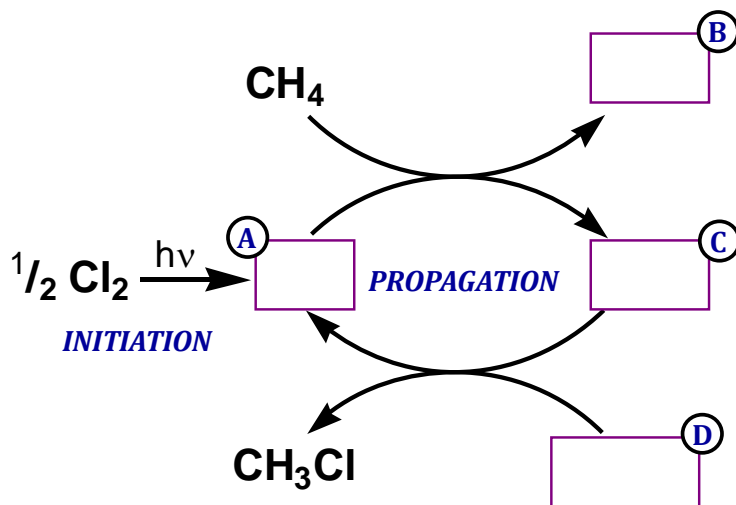
(C) Net Reaction

(D) Termination

Notes

Lecture Topic III.18: Radicals II
Radical Halogenation of Alkanes

... or we can write a simple cycle (shows **initiation** and **propagation** but not **termination**):




Termination occurs when any two radicals come together.

Notes

Only Cl_2 and Br_2 are commonly used in this radical chain reaction because fluorine is too reactive and iodine is not reactive enough. The structure of the alkane we use also plays an important role.

The key step is the homolytic cleavage of the alkane C-H bond to form the radical:



Easier radical formation	BDE Trends:	
	<u>Structure</u>	<u>BDE</u>
	$\text{CH}_3\text{—H}$	104 kcal
	$\text{CH}_3\text{CH}_2\text{—H}$	98 kcal
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—H}$	98 kcal (1°)
	$(\text{CH}_3)_2\text{CH—H}$	95 kcal (2°)
	$(\text{CH}_3)_3\text{C—H}$	91 kcal (3°)

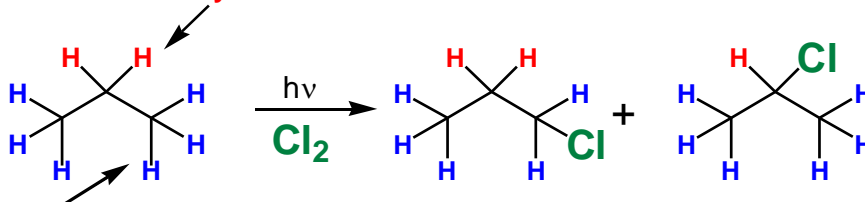
The take-home lesson is:

Ⓐ

Notes

Lecture Topic III.18: Radicals II
 Radical Halogenation of Alkanes

there are 2 secondary H atoms



there are 6 primary H atoms

Experimentally observed:	43%	57%
Statistically anticipated:	75%	25%

We observe a greater than statistically anticipated reactivity at the secondary site. The reaction has a greater **regioselectivity** for this site.

We already know that the secondary radical is more stable than the primary, and that the secondary C-H bond has a lower BDE, so this regioselectivity makes sense.

Notes

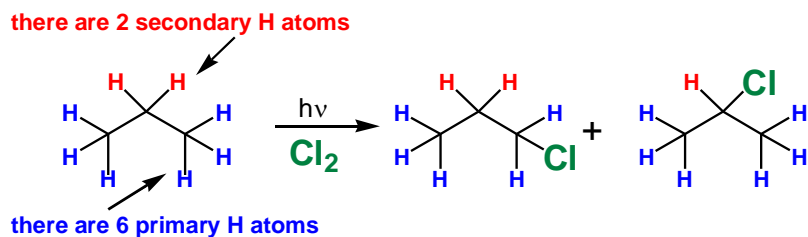
Lecture Topic III.18: Radicals II

Radical Halogenation of Alkanes

When Cl_2 is used, the relative reactivity can be approximated as:

Relative Reactivity of C-H:	3°	2°	1°
	5.2	3.9	1

Use this to predict product distribution for the chlorination of propane:



Rel. amount of 1° product = reactivity of 1° H x number of 1° H's

Rel. amount of 2° product = reactivity of 2° H x number of 2° H's

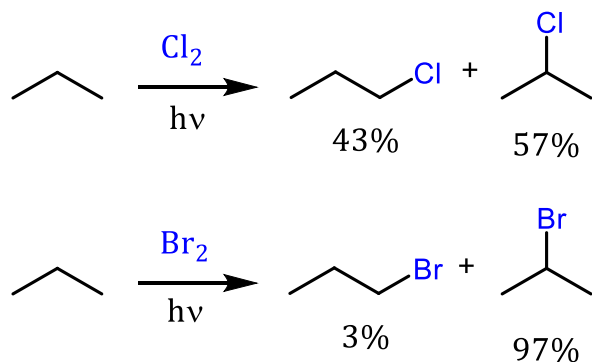
$$= 3.9 \times 2 = 7.8 = 43\% \text{ primary}$$

$$= 1 \times 6 = 6 = 57\% \text{ secondary}$$

Notes

Lecture Topic III.18: Radicals II
Radical Halogenation of Alkanes

Bromine is less reactive and therefore more **selective** than chlorine. Consider the observed products for these reactions:



From these data we can deduce that the selectivity of bromine must be more pronounced than for chlorine. This is the case:

Site:	3°	2°	1°
Relative reactivity:	1640	82	1

Notes