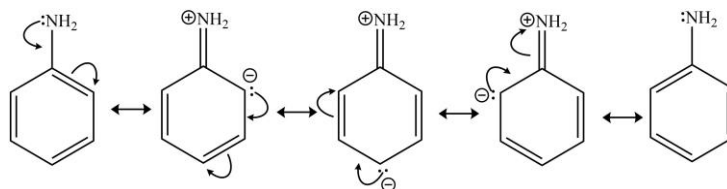


❖ Effect of Structure on Reactivity

When chemical equations are used to represent chemical reactions, functional groups are usually represented as a condensed formula because all the compounds with a particular functional group give more or less the same products. It enables us to categorize a large number of reactions in the same class for a better understanding and memorization. However, it must be kept in mind that two compounds with the same functional group may react in an entirely different manner because the structure of the rest of the molecule affects the overall reactivity at the corresponding functional group. Moreover, even if the two compounds with the same functional group undergo the same reaction, their rate rates may be slightly or largely different. The effects of molecular structure on the overall reactivity can be fragmented into three main classes; resonance or mesomeric effect, inductive effect, and steric effect. Now although we see a combined result of two or all three phenomena in most of the cases; it is still possible to extract information about their individual effects. A brief idea of all the three effects of molecular structure on reactivity is discussed below.

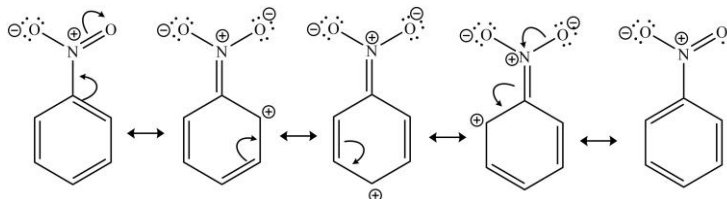
➤ Impact of Resonance Effect on Reactivity

The resonance or mesomeric effect in organic compounds may affect the reactivity up to a great as it can produce polarity by creating centers of high and low electron density. For instance, +R groups increase the electron density at *o*- and *p*- positions making them more susceptible to attacking electrophile.



It is also worthy to mention that groups showing the +R effect are having lone pair of electrons that can be put into conjugation with the double of the chain or ring to which it gets attached with. Some of the typical groups showing +R effect are $\text{O}^- > \text{NH}_2 > \text{NHR} > \text{OR} > \text{NHCOR} > \text{OCOR} > \text{Ph} > \text{F} > \text{Cl} > \text{Br} > \text{I}$

Similarly, groups with the –R effect tends to decrease the electron density at *o*- and *p*- positions in the benzene ring making the *m*-position more susceptible towards attacking electrophile.

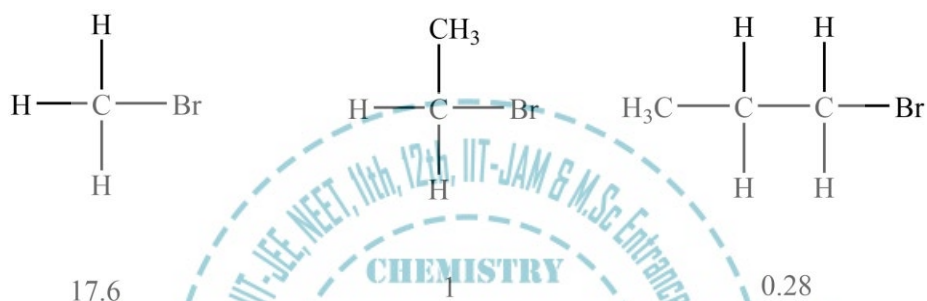


It is also worthy to mention that groups showing the –R effect are having a double bond that can be put into conjugation with the double of the chain or ring to which it gets attached with. Some of the typical groups showing –R effect is $\text{NO}_2 > \text{CN} > \text{S(=O)}_2\text{OH} > \text{CHO} > \text{C=O} > \text{COOCOR} > \text{COOR} > \text{COOH} > \text{CONH}_2 > \text{COO}^-$. It is also worthy to recall that the alkyl groups, which do not have multiple bonds or unshared pairs, can also show the +M effect due to hyperconjugation.

➤ **Impact of Inductive Effect on Reactivity**

The inductive effect in organic compounds may affect the reactivity up to a greater as it can produce polarity by its electron-donating or electron-withdrawing ability. For instance, groups with the +I effect tend to increase the electron density and making them less or more stable or susceptible to attacking electrophile. Relative inductive effects have been experimentally measured with reference to hydrogen, in increasing order of +I effect or decreasing order of -I effect, as follows:

$-\text{NH}_3^+ > -\text{NO}_2 > -\text{SO}_2\text{R} > -\text{CN} > -\text{SO}_3\text{H} > -\text{CHO} > -\text{CO} > -\text{COOH} > -\text{COCl} > -\text{CONH}_2 > -\text{F} > -\text{Cl} > -\text{Br}$
 $> -\text{I} > -\text{OR} > -\text{OH} > -\text{NR}_2 > -\text{NH}_2 > -\text{C}_6\text{H}_5 > -\text{CH}=\text{CH}_2 > -\text{H}$ and $\text{C}-\text{H} < \text{C}-\text{D} < \text{C}-\text{T}$ in increasing order of +I effect, where H is Hydrogen and D or T are hydrogen's isotopes.



Relative rates of reaction of RBr with ethanol

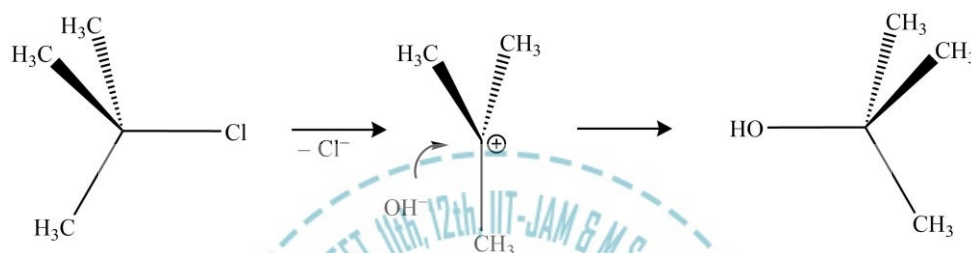
The inductive effect is extremely useful to describe the molecular stability depending on the sign and magnitude of the charge present on the atom and the substituent that is attached to this atom. For instance, if an atom carries a positive charge and binds to a group with -I effect, its charge becomes 'boosted' and the molecule tends to be less stable. Likewise, if an atom carries a negative charge and binds to a group with +I effect, its charge will also get 'amplified' making it less stable. Conversely, if an atom has a positive charge and binds to a +I effect, its charge will get 'de-boosted' and therefore, the molecule will become more stable. Similarly, if an atom has a negative charge and is attached to a -I group its charge becomes 'de-amplified' and the molecule will get more stable. The attribution can be found for such behavior in the fact more charge on an atom cuts stability and less charge on an atom raises the stability.

The basicity and acidity of a molecular species are also affected by the inductive effect. If substituents with +I inductive effect are attached to a molecule, the electron density at the donor site increases, which in turn, makes it more basic. Likewise, if substituents with -I inductive effect are attached to a molecule, the electron density at the acceptor site decreases, which in turn, makes it more acidic. Furthermore, the acidity also increases as the number of -I groups attached to a molecule increases; and the same is true for bases since the increased number of +I groups on a molecule increases its basicity.

It is also worthy to recall that some groups can also affect the reactivity in the same way as an effect but through space i.e. field effect.

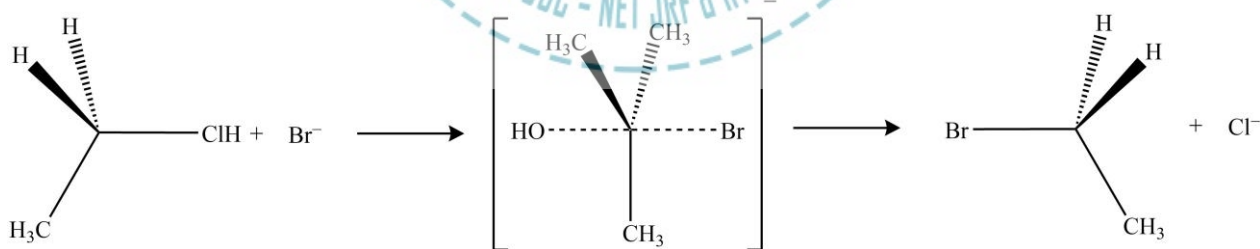
➤ **Impact of Steric Effect on Reactivity**

The steric effect in organic compounds may affect the reactivity up to a greater extent by affecting the stability of reactants, intermediates, or transition states. These effects are primarily of nonbonding interactions that affect the reactivity and conformation of various ions and molecules. Also, these effects also couple with electronic effects which usually govern reactivity and shape. Steric effects primarily arise from repulsive interactions between overlapping electronic clouds. These effects are largely employed in academic and applied chemistry for many purposes. For instance, the reaction-rate increases with the increase in bulky groups in the S_N1 pathway.



Steric effects also give rise to steric hindrance which slows down the chemical reactions due to bulk presence. Nevertheless, it should be kept in mind that steric hindrance is primarily an intermolecular phenomenon, whilst the dialogue of steric effects usually emphasizes intramolecular interactions. The steric hindrance is mainly employed to dictate the reaction selectivity like slowing down unwanted concurrent reactions.

Also, the steric hindrance between *cis* substituents can disturb the torsional bond angles; and is responsible for the observed profile of rotaxanes and the small rates of racemization of compounds like 2,2'-disubstituted biphenyls and their derivatives. The rate of reaction also increases with the decrease in the number size of bulky groups in the S_N2 pathway.



Comparative reaction rates give a very useful vision into the effects of the steric bulk of different groups. When standard experimental conditions were used, the solvolysis of methyl bromide is 10^7 times faster than what in neopentyl bromide. The variance shows the oppose of attack on the substrate with the sterically bulky $(CH_3)_3C$ substituent. These values (resulting from equilibrium measurements of monosubstituted cyclohexanes) provide another measure of the bulk of various substituents. Also, the bulk of a substituent can be measured by the extent that it favors the equatorial position.

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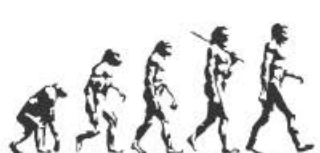
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC – NET JRF, IIT-GATE)

Founder & Educator, Dalal Institute

E-Mail: dr.mandeep.dalal@gmail.com

www.mandeepdalal.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

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