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Relationship between thermodynamics and the rate of organic reaction (Open discussion)

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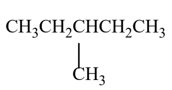
DISCUSSION

Organic chemistry is the chemistry of thermodynamic (TD) functions, Gibbs free energy and the action of entropy, from which all processes are derived. Any stress observed within the molecules of organic compounds arise from mutual interatomic actions, Gibbs energy and action entropy, bond polarization, charge density, dissipation, scattering, Baier stress, van der Waals forces, electron donor and acceptor groups, mesomerism, tautomerism, configuration, conformation *etc*.

The TD properties are state functions that involves enthalpy, internal energy, entropy etc. Gibbs energy is the internal energy of the compound and is one of the forms of the thermodynamic potential. The higher the internal stress of molecules, the higher is the Gibbs energy. In the case of van der Waals impulse the TD stability of the compound will be lost and the standard entropy will be an equilibrium indicator:

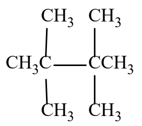
$CH_3(CH_2)_6CH_3$

(111)



$CH_3CH_2CH(CH_3)CH_2CH_3$

109.5



$CH_3C(CH_3)_2-C(CH_3)_2CH_3$

94

The organic reaction rate and the yield of the product depend on the action of the TD functions. In this context the organic reaction is different from the ionic reaction. The organic reaction does not occur directly but proceeds through intermediate states (IM) because the covalent bond has definite energy:

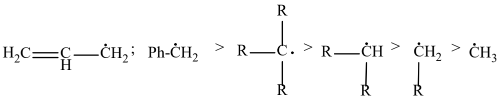
$$A + B \longrightarrow IM \longrightarrow C$$

The IM has a large chemical potential because they exist mostly as free radicals such as S_R-reactions, carbocations or A_E, S_E, S_N, E1 reactions.

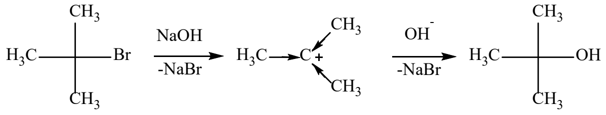
The faster the IM formation rate, the faster the reaction rate, (if the rate of decomposition of the IM is faster than their formation). However, the reaction rate and IM formation rate depend on the following factors:

- TD stability of the IM
- TD stability of the IM free energy decrease and entropy increase
- The free energy decrease of the free radical, the charge dispersibility for the carbocation (CC) and the decrease in the charge force
- The charge force decrease of the free radical, CC alkylation, phenylation, vinylation and mesomerism.

The formation rate sequence and the TD stability of the IM (free radical, CC):

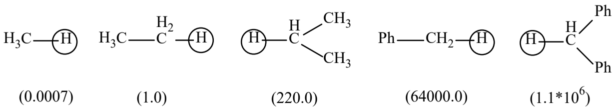


Since it is an electronic donor, the alkali group will have an effect. Thus, tertiary butyl bromide (1,1-dimethylbromoethane) will enter into an Sn1 reaction $1×10^6$ times faster than bromoethane.



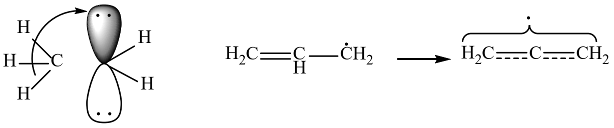
Here especially, the phenyl, vinyl group will exert a stronger influence on the DT stability and formation rate of the IM because their structures are mesomeric. A strong dissipation or scattering of internal action and charge of the IM is also affected by a mesomeric structure.

The reaction rates of the following compounds for S_R-reaction by bromide are:

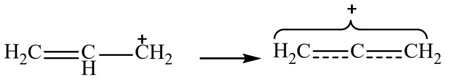


Influence may be exerted upon the IM reaction rate by the implantation of an electron donor and acceptor group in the phenyl cycle i.e., addition of a catalyst.

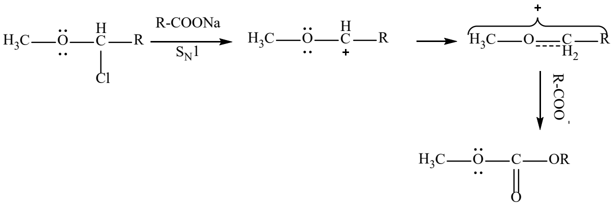
The free radical (IM) formed as a result of an S_R-reaction will be stabilized by a π-p bond with a π-link and a p-σ bond with a C-H link (hyperconjugation) respectively, because in these cases the octet is more likely to be filled:

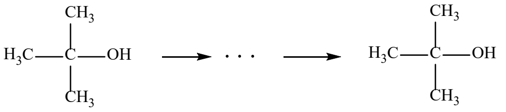


So on stabilization, the propylene and toluene products will be formed 100 million times faster in the Sr-reaction. The IM formed from the chlorite allyl and benzyl will be transferred into the mesomer form and also stabilized. The π-link will be dispersed into the vacant space and attracted by the very powerful CC electron acceptor. Moreover, the IM (CC) formed from the chloride allyl and benzoyl will be transferred into the mesomer and spontaneously stabilized:



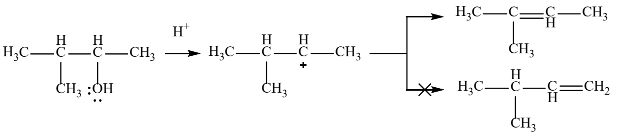
The shared pair of free electrons will also exert a strong influence on the reaction rate of nucleophile displacement. For example:





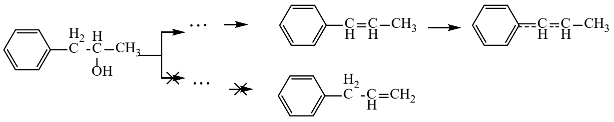
Here, the “a”-reaction progresses 1×10^9 times faster than the “b”-reaction and the resulting IM is 1×10^9 times as stable than b-reaction.

As far as the “b”-case is concerned, the methyl group exerts an influence upon the IM-CC stabilization.



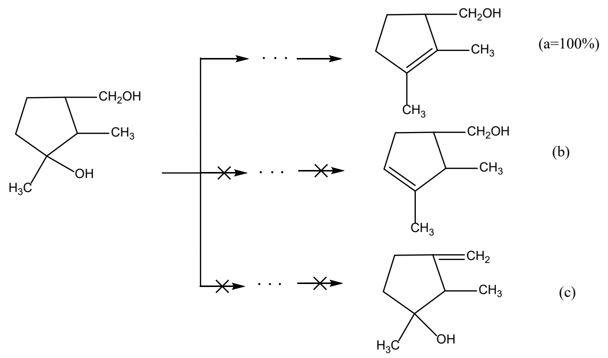
In regard to its donor nature, the stereochemistry factor exerts a negative influence. The stabilized one as far as TD will be forced forcibly, above all else from the reaction. The reaction yield depends on the TD stabilization of the forming compounds (a, b, c-reactions):

The trimethylethylene (2-methylbut-2-ene) has a lower activation energy and stability in regard to the TD and therefore it will be formed faster because the π-link entered into the hyperconjugation of whole C-H bonds of methyl groups.



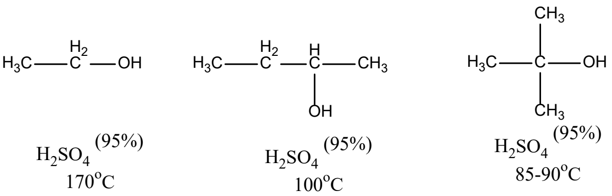
The mesomeric structure will be formed 100 percent because it has low Gibbs’s energy and stability as far as the TD is concerned.

c. Dehydration of 1,2-dimethyl-3-methylcyclopenthanol:



The reaction rate will be higher because both the IT and the final product have stability in regard to the TD in the a-compound reaction, low Gibbs energy and high entropy. The formation of b, c- compounds will be closed in regard to the TD.

A spirit’s dehydration: the formation rate of the oxonium ion → CC → final product depends on the alkylation of carbonyl group. Activation energy will be decreased and reaction will be easier:



From the previous analysis, the following is a new open discussion point which is being presented:

“When the IM and final product of reaction in regard to TD is stable, the Gibbs free energy is low and entropy is higher, then the reaction rate will be higher and the activation energy will be lower.” Presently, the rate of organic reaction has been explained as a concentration change. Even if it is considered as a classic explanation, it is insufficient to be explained as “origin compound is active”. The reason in this case remains unclear, not withstanding a basic explanation of reaction rate of organic compound, which is completely different from the ionic compound.

The explanation of reaction rate is necessarily connected to the TD- function, because chemical activation of any compound depends on internal potential energy. From the point of the TD a chemical reaction is a result of energy exchange of particles in reaction.

To the best of author's knowledge, there are no references on the organic reaction rate with the thermodynamic stability of the IM and final products, except a few chemical study books which mentioned about such possibility [1, 2]. Therefore, the discussion point is considering by myself as a new finding.

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2. Reid K. (1972) Course of physical organic chemistry. Publishing house, Mir, 185. (In Russian)