Details of Module

| Subject	Chemistry
Course Name	M. Sc. Ist Semester
Paper No.	Core Course III (Organic Chemistry-I)
Module Name/Title	Aromatic electrophilic substitution (Lect.-2)
Course Teacher	Mithilesh Kumar Singh Assistant Professor Department of Chemistry T. P. College, Madhepura B. N. Mandal University, Madhepura
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(1) Energy profile diagram

When we consider the thermodynamics of the two mechanism steps, one feature is obvious. Electrophilic attack on the benzene ring (first step) disrupts aromaticity. Deprotonation of the arenium ion (second step) restores aromaticity. Aromaticity is a significant stabilizing feature, and its loss is energetically expensive. Thus we expect $\Delta G^{\ddagger}$ for the

electrophilic attack step to be higher than $\Delta G^{\ddagger}$ for the deprotonation step. By this logic we predict that electrophilic attack is the rate-determining step. (This analysis ignores other energy changes such as loss and formation of bonds.) Experimental kinetic evidence confirms that the electrophilic attack step is rate determining. This suggests that either aromaticity is in fact the deciding thermodynamic factor or the bond energy analysis gives the same result.

Now that we know the rate-determining step we can draw the energy profile.

Reaction coordinate
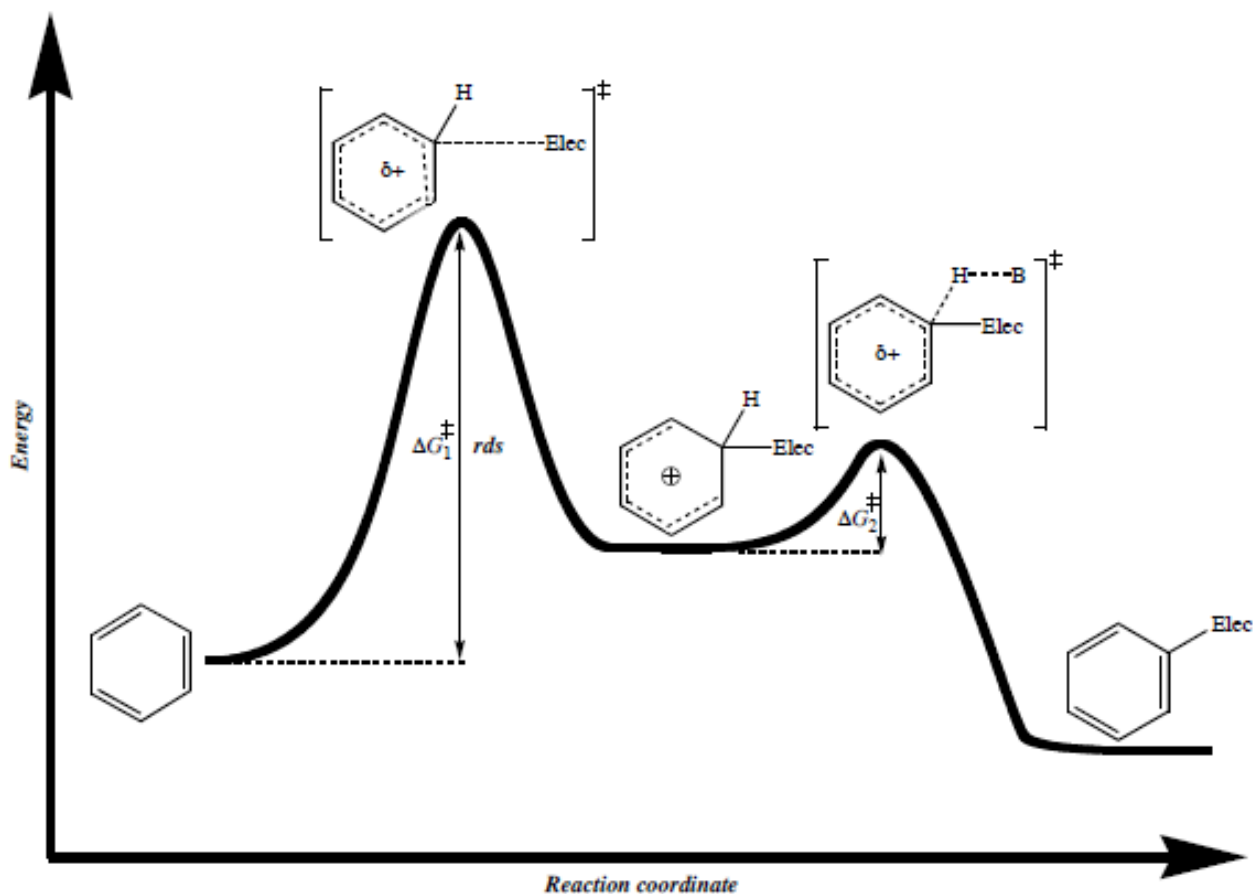
(1) The energy diagram of this reaction shows that step 1 is highly endothermic and has a large $\Delta G^{\ddagger}_1$.

(2) The first step requires the loss of aromaticity of the very stable benzene ring, which is highly unfavourable.

(3)The first step being a slow step, is rate-determining .

(4) Step 2 is highly exothermic and has a small $\Delta G^{\ddagger}_2$ The ring regains its aromatic stabilization, which is a highly favorable process.
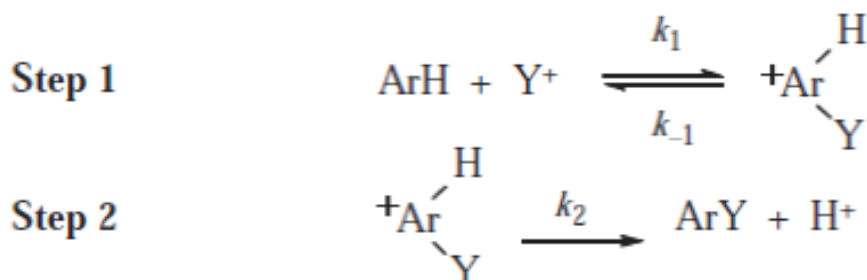
(2) Evidence in favour of Arenium ion mechanism

The evidence for the arenium ion mechanism is mainly of two kinds:

(1) Isotope Effects:

If the hydrogen ion departs before the arrival of the electrophile (S_E1 mechanism) or if the arrival and departure are simultaneous, there should be a substantial isotope effect (i.e., deuterated substrates should undergo substitution more slowly than non-deuterated compounds) because, in each case, the C−H bond is broken in the rate-determining step . However, in the arenium ion mechanism, the C−H bond is not broken in the rate-determining step, so no isotope effect should be found. Many such studies have been carried out and, in most cases, especially in the case of nitrations, there is no isotope effect. This result is incompatible with either the S_E1 or the simultaneous mechanism. However, in many instances, isotope effects have been found. Since the values are generally much lower than expected for either the S_E1 or the simultaneous mechanisms (e.g., 1–3 for k_H/k_D instead of 6–7), there must be another

explanation. For the case where hydrogen is the leaving group, the arenium ion mechanism can be summarized:

Step 1 $\qquad$ $ArH + Y^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^+Ar{\overset{H}{\underset{Y}{\diagup}}}$

Step 2 $\qquad$ ${}^+Ar{\overset{H}{\underset{Y}{\diagup}}} \xrightarrow{k_2} ArY + H^+$

$\qquad$ The small isotope effects found most likely arise from the reversibility of step 1 by a *partitioning effect*. The rate at which $ArHY^+$ reverts to ArH should be essentially the same as that at which $ArDY^+$ (or $ArTY^+$) reverts to ArD (or ArT), since the Ar−H bond is not cleaving . However, $ArHY^+$ should go to ArY faster than either $ArDY^+$ or $ArTY^+$, since the Ar−H bond is broken in this step. If $k_2 \gg k_{-1}$, this does not matter; since a large majority of the intermediates go to product, the rate is determined only by the slow step ($k_2[ArH][Y^+]$) and no isotope effect is predicted. However, if $k_2 \leq k_{-1}$, reversion to starting materials is important. If k_2 for $ArDY^+$ (or $ArTY^+$) is $<k_2$ for $ArHY^+$, but k_{-1} is the same, then a larger proportion of $ArDY^+$ reverts to starting compounds. That is, k_2/k_{-1} (the *partition factor*) for $ArDY^+$ is less than that for $ArHY^+$. Consequently, the reaction is slower for ArD than for ArH and an isotope effect is observed.

## 2. Isolation of Arenium Ion Intermediates:

$\qquad$ The isolation of arenium ions in many cases provides for a very strong evidence for the arenium ion mechanism. When 10 was heated, the normal substitution product (11) was obtained. Even the simplest such ion , the benzenonium ion (12)

has been prepared in HF−SbF$_5$ − SO$_2$ClF−SO$_2$F$_2$ at -134 °C, where it could be studied spectrally.
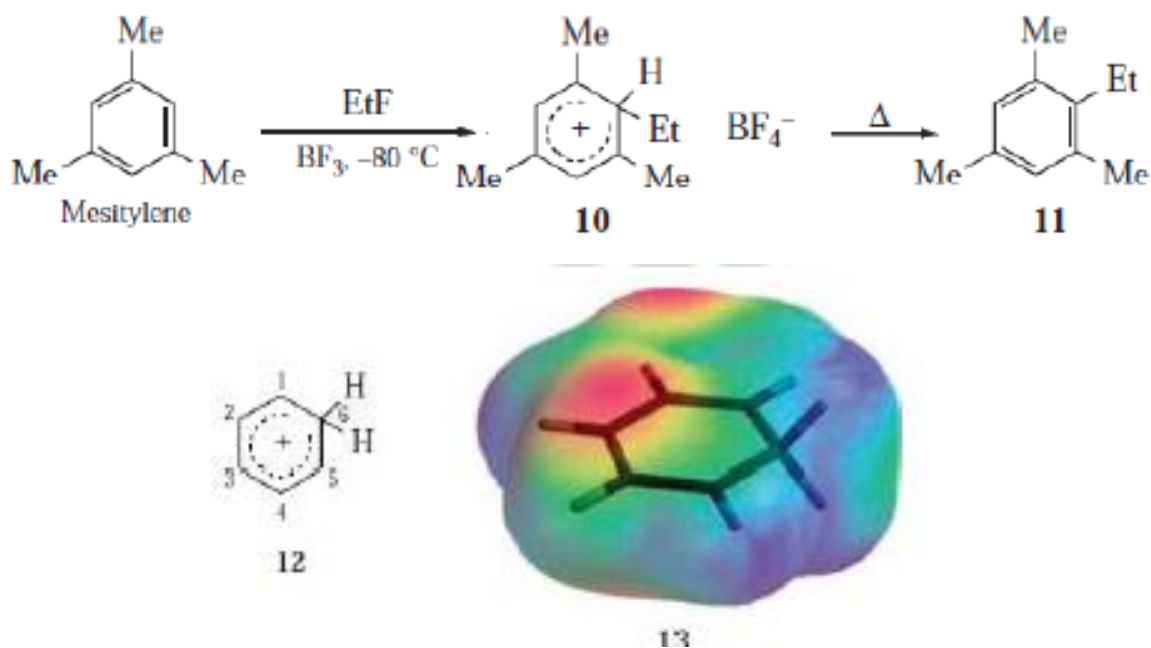
(3) NMR spectroscopy evidence

The direct evidence for proposed reaction intermediate in aromatic substitution has been obtained by Dr. Olah using NMR spectroscopy. A mixture of mesitylene (1) with an alkyl halide and a good lewis acid at low temperatures yielded the intermediate (2). This (2) went on to the final product (3) at higher temperature.
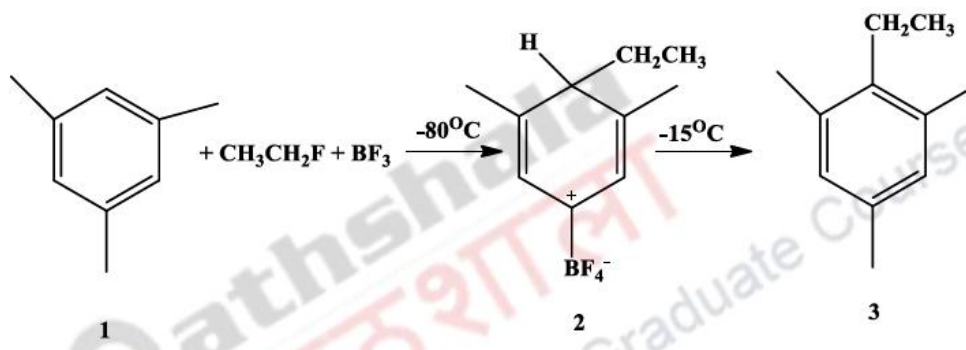
There are numerous studies which show that such salts like this intermediate can exist as stable species under favourable

conditions. Even the simplest benzonium ion (4) could be prepared and studied. These types of charged units are sometimes called as σ complexes.

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