

## 11.2: Background

In lecture we learned that substituent groups to benzene rings can influence the regiochemistry of an electrophilic aromatic substitution (EAS) reaction. These groups behave differently depending on whether they are withdrawing or donating electron density into the aromatic system. During an aromatic substitution reaction an initial nucleophilic attack by an arene results in a resonance-stabilized carbocation intermediate known as a  $\sigma$  (sigma) complex. If the substituent on an arene has the ability to donate electron density into the arene ring, it is able to stabilize the carbocation of a  $\sigma$  complex, but only if the incoming electrophile adds ortho or para to the existing substituent.

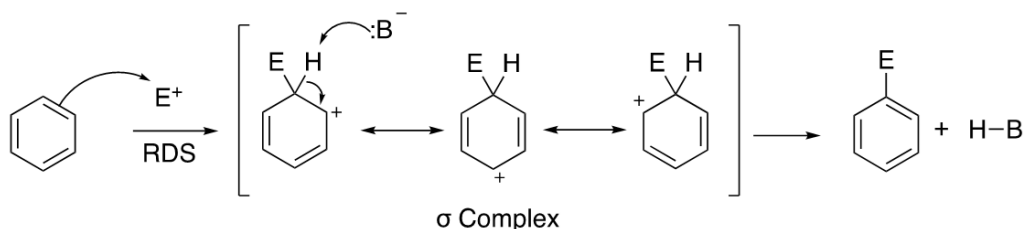


Figure 1. Electrophilic aromatic substitution mechanism illustrating rate determining generation of the  $\sigma$  complex

The ability of a methoxy group to direct EAS regioselectivity is shown in Figure 2. When an incoming bromine electrophile is added ortho or para to a methoxy group, a  $\sigma$  complex is created where the lone pairs on oxygen can help to stabilize the carbocation via resonance. In fact, there is a resonance structure created where all atoms obey the octet rule. However, if an incoming bromine electrophile adds to the meta position, the carbocation of the  $\sigma$  complex is unable to be stabilized via resonance. When a base in solution removes a proton and restore aromaticity, the dominant products of this reaction are ortho and para substituted.

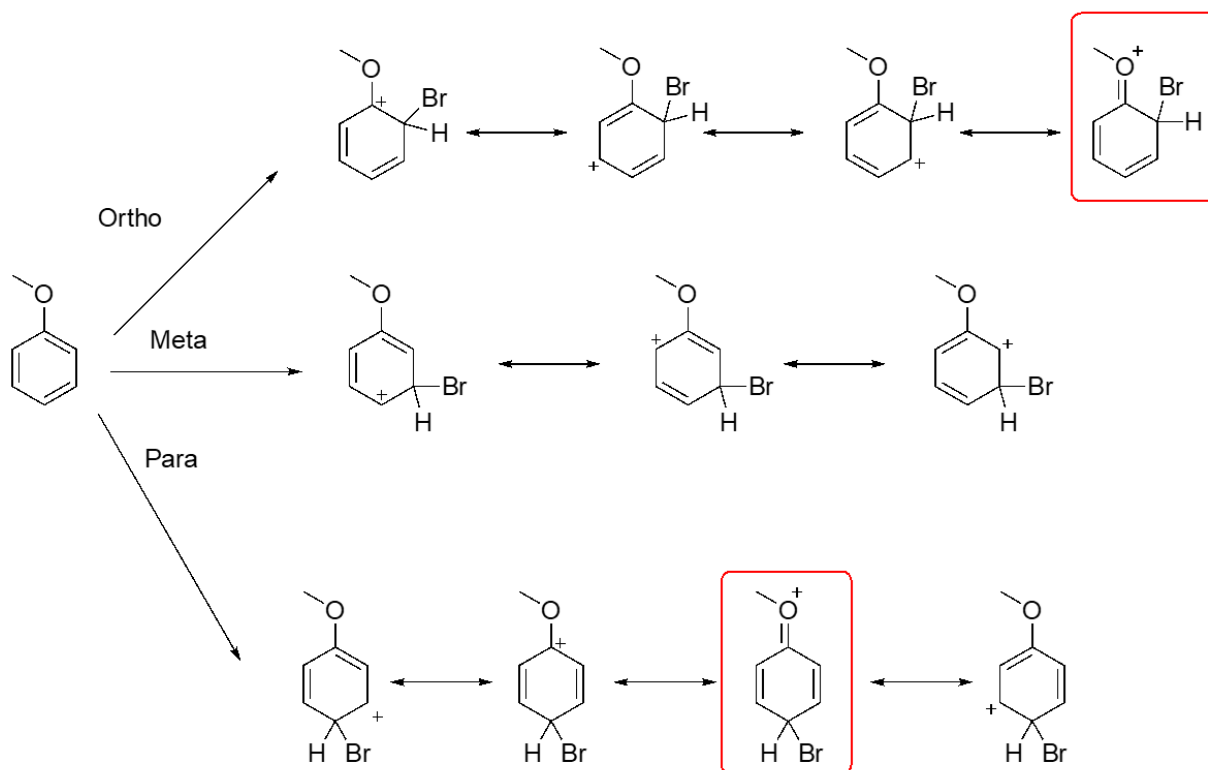


Figure 2. Addition of a bromine electrophile to anisole (methoxy benzene). Please note how resonance stabilization of the carbocation by the methoxy group only occurs with ortho or para substitution. Resonance structures utilizing this additional stabilization, and thus generating a resonance structure where all atoms are obeying the octet rule are indicated by red boxes.

A similar analysis of the addition of a bromine electrophile to an arene with an electron withdrawing substituent yields different results. As shown in Figure 3, when an incoming bromine electrophile is added ortho or para to the ammonium (positive nitrogen)

substituent, a  $\sigma$  complex with a resonance structure is created with two adjacent positive charges. This highly energetic arrangement makes addition para and ortho to an electron withdrawing group difficult. On the other hand, if an incoming bromine electrophile adds meta to the ammonium group the  $\sigma$  complex created does not allow for the carbocation to be formed adjacent to the electron withdrawing group. This difference in stability makes it easier for an incoming electrophile to add meta rather than ortho/para to a withdrawing substituent.

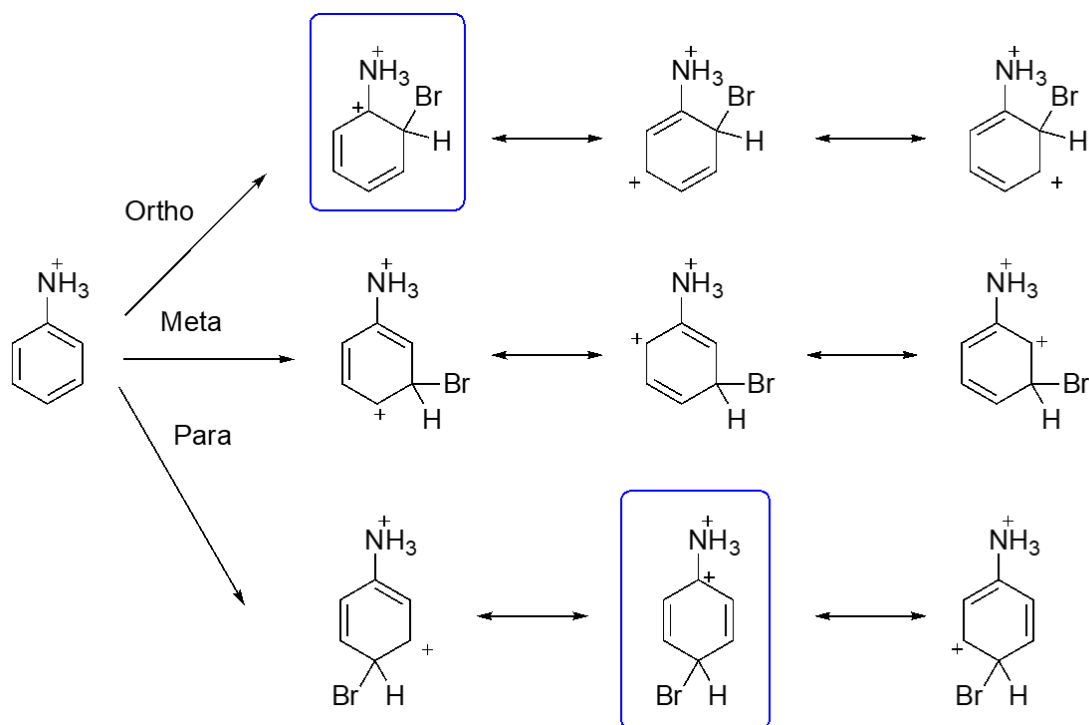


Figure 3. Addition of a bromine electrophile to the anilinium ion. Please note that addition of the electrophile to the ortho or para position creates a high energy  $\sigma$  complex with two adjacent positive charges (indicated by a blue box). When the electrophile adds to the meta position, the two positive charges cannot be placed adjacent to one another.

Generation of the  $\sigma$  complex is the rate-determining or most difficult step of the substitution reaction and the magnitude of the  $\Delta G^\ddagger$  of this reaction directly correlates with the rate of the reaction. Via the Hammond postulate, the transition state of a reaction step resembles the species that is closest to it in energy. The more unstable the  $\sigma$  complex is, the higher in energy the transition state will be. A higher energy transition state will decrease the rate at which product is formed via that pathway. Put more simply, the higher energy  $\sigma$  complexes will be formed more slowly, resulting in less product formed via that pathway.

In the exercise that follows you will examine the energy levels of various  $\sigma$  complexes and transition states leading to the  $\sigma$  complexes to probe the origin of ortho, meta, and para selectivity.

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