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Electron donating groups list pdf

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The importance of understanding electrophilic aromatic substitution reactions lies not only in their specific applications but also in the broader concepts they represent. To grasp these reactions, it's crucial to understand resonance and electronegativity, which are key concepts that can affect the rate of these reactions. Electrophilic aromatic substitution (EAS) is a type of reaction where an electrophile replaces one of the hydrogen atoms on an aromatic ring. The speed at which this occurs is influenced by the electron-richness of the aromatic ring and the presence of substituents. Groups that can donate electron density to the ring accelerate EAS reactions, making them activating groups if they increase the rate relative to a hydrogen atom. Conversely, deactivating groups decrease the rate. A critical aspect often misunderstood at first is that certain groups seemingly expected to be deactivating due to their electronegativity can actually act as activators through resonance, allowing a lone pair of electrons to donate into the ring. This demonstrates how complex and nuanced these reactions can be, requiring detailed experimental measurements to accurately determine their rates and mechanisms. The mechanism behind EAS reactions involves forming and breaking bonds on the same carbon atom, with specific identities like bromination, chlorination, nitration, sulfonylation, Friedel-Crafts alkylation, and Friedel-Crafts acylation. While a general understanding of these reactions can be taught in introductory courses, determining their exact mechanisms often involves extensive lab work to test hypotheses. Measuring reaction rates is a valuable tool for understanding the mechanism of EAS reactions. By analyzing how slight changes in experimental conditions affect the rate, scientists can gain insights into how these reactions operate at a molecular level. This includes changing the substrate (reactant), temperature, and solvent, which can provide crucial information about the reaction's pathway. Understanding electrophilic aromatic substitution reactions is not only about mastering specific reactions but also about appreciating the underlying principles that govern their occurrence. By delving into resonance, electronegativity, and the intricacies of measuring reaction rates, chemists can gain a deeper understanding of these complex processes. Tuning Electrophilicity through Substitution: A Study on Nitration Reactions Electron-rich and electron-poor substituents can significantly impact the rate of electrophilic aromatic substitution reactions, such as nitration. By examining the effects of different substituents on benzene derivatives, researchers have identified a general pattern that holds true for various electrophilic aromatic substitution reactions. When a hydrogen atom is replaced by a methyl group in benzene to form toluene, the nitration reaction rate increases by 23 times compared to the original benzene. Conversely, replacing a hydrogen with a trifluoromethyl group results in a 40,000-fold decrease in reaction rate. This pattern suggests that electron-donating groups like CH3 accelerate the reaction, while electron-withdrawing groups such as CF3 decelerate it. The definition of "activating" and "deactivating" groups is based on their effect on the reaction rate relative to hydrogen. Activating groups increase the rate of nitration, whereas deactivating groups decrease it. The methyl group, being an electron-donor, falls under this category, while the trifluoromethyl group serves as an electron-withdrawing agent. The observed effects can be attributed to inductive effects, specifically "sigma" (σ) donation and acceptance. CH3 is considered an electron-rich species due to its electronegative carbon atom, which donates a partial negative charge, making it an effective electron donor. In contrast, the trifluoromethyl group has a highly electronegative fluorine atom, pulling electron density away from the carbon atom and resulting in an electron-withdrawing effect. We typically view CF3 as an electron-poor species, acting as an electron acceptor due to its inductive effect. This sigma accepting behavior is sometimes referred to as "sigma donation" or "sigma acceptance". Considering the activating and deactivating effects of different groups on electrophilic aromatic substitution, we can hypothesize that electron-donating groups are activating (relative to H), while electron-withdrawing groups are deactivating (relative to H). In terms of resonance, pi donors and acceptors help us understand how alkyl groups influence this process. Now, let's explore the effects of other functional groups on electrophilic aromatic substitution. For instance, what about a hydroxyl group (-OH) and its potential impact on the rate of nitration? Do you think -OH would be activating or deactivating? Based on our previous discussion, it's logical to assume that -OH would be deactivating due to oxygen's high electronegativity and sigma-accepting properties. However, in reality, -OH greatly accelerates the reaction rate, making it an extremely activating group. Clearly, there must be additional factors at play beyond the inductive effect of oxygen. Oxygen and nitrogen-containing lone pairs are highly activating when bonded directly to the ring. Hydroxyl groups are excellent pi donors due to their ability to form a pi bond with adjacent atoms containing available p-orbitals. This resonance donation effect overcomes electron withdrawal via inductive effects, explaining why hydroxyl groups are activating. The same is true for nitrogen-containing lone pairs like amines and amides. In contrast, halogens (F, Cl, Br, I) tend to be deactivating due to their strong sigma-accepting properties. Alright, let's flip things. What if electrons flow in the opposite direction? You know what the opposite of "pi-donor" is – "pi-acceptor". Certain groups can accept pi bonds from the ring, resulting in new lone pairs on substituent atoms. Examples are NO2, carbonyl (C=O), sulfonyl, cyano (CN) and others. These groups universally deactivate electrophilic aromatic substitution, slowing reaction rates. In terms of resonance, we draw a pi bond between the aromatic ring and an atom bound to it, forming a new lone pair on an electronegative atom, leaving a positive charge on the ring. To keep things straight, think of five main "buckets". Nitrogen and oxygen atoms with lone pairs (amines, phenol) are strong activating groups due to pi-donation. Alkoxy, amide, ester groups less strongly activate, while alkyl groups moderately activate through inductive effect. Halogens moderately deactivate, and NO2, CN, SO3H, CHO, COR, COOH, COOR, CONH2 groups strongly deactivate as pi-acceptors. Electron withdrawing groups with no lone pairs (CF3, CCl3, NR3+) are also strongly deactivating. Once you grasp that O and N-bonded functional groups with lone pairs activate, and halogens deactivate, the rest is fairly straightforward. Our table of activating and deactivating groups resembles a pKa table – we can identify factors affecting activation or deactivation, but in the end, it comes down to experimental measurements of reaction rates. Electrophilic aromatic substitution mechanisms typically involve unstable electron-poor species like carbocations, where tertiary carbocations are more stable than secondary or primary ones due to alkyl group stabilization and electron-withdrawing group destabilization. Adjacent atoms donating lone pairs through resonance also stabilize carbocations, while pi acceptors can destabilize them. A common first step in understanding these mechanisms involves the electrophilic aromatic substitution process itself, which breaks a C-H bond. Using deuterium labelling to probe this mechanism shows no significant deuterium isotope effect, suggesting that C-H bond breakage isn't the rate-determining step. Carbocation intermediates have been isolated in reactions like Friedel-Crafts alkylation, further supporting proposed mechanisms. The stability of fluorine as an activator in electrophilic aromatic substitution can be attributed to its strong pi-bond with carbon, and some reactions may exhibit small deuterium isotope effects due to partitioning effects. Various studies have explored the effects of substituents on the reactivity of benzene derivatives in electrophilic aromatic substitution reactions. A paper detailing the distribution of ortho/para products from anilides via chlorination (typically 65% para and 35% ortho) failed to compare rates with benzene, however. Research by Bradfield and Jones (1941) on kinetics and mechanisms for some electrophilic benzene substitution reactions provided partial rate factors for nitration of benzene and related compounds in Table I, showing chlorobenzene and bromobenzene are around 1-3% as reactive as benzene, while ethyl benzoate is significantly deactivated at about 0.1-0.2%. Toluene, on the other hand, was found to be 40-50 times more reactive than benzene. Studies by Robertson et al. (1953) further detailed the reaction rates of halogenation for various benzene derivatives, highlighting a wide range from extremely activating (N,N-dimethylaniline being 1018 times more reactive) to deactivating substituents (nitrobenzene being 10^-6 times less reactive). Another study by de la Mare and Vernon (1951) examined the influence of the methoxyl group in aromatic substitution, with anisole showing an overall reactivity 108 times higher than benzene. However, this increased reactivity led to a very low o/p selectivity in reactions. A more rigorous study by Stock and Brown (1960) found that bromination of anisole produced a high o/p selectivity, with 1.6% ortho and 98.4% para products, and measured the relative reaction rate of anisole to benzene as 1.79 x 10^9:1.00. The study also demonstrated the comparability of s+ values (electrophilic Hammett constants) measured through various methods and their ability to predict the effect of substituents on electrophilic aromatic substitution reactions. Finally, Ingold et al.'s work (1931) introduced the concept of partial rate factors in the nitration of toluene, showing its reactivity could vary from 1.2 to 10 times that of benzene. This text discusses various papers on nitration reactions and the effects of different substituents on aromatic systems. A key finding is that t-butylbenzene is much more p-directing than toluene due to steric factors, leading to a higher percentage of para-nitration products. The paper also highlights the transmission of polar effects through aromatic systems and the influence of directing groups on nuclear reactivity. Notably, the nitration of halogenobenzenes shows that chlorobenzene and bromobenzene are much less reactive than benzene, with an empirical reactivity difference of around 25-fold. Additionally, the paper discusses the deactivating nature of the nitro group in mononitrotoluenes, which can override the activating effects of other substituents. The text also touches on the effects of positive poles in aromatic substitution, including the deactivation of anilinium ions compared to aniline. Furthermore, it explores the electrophilic nitration and halogenation of trifluoromethoxybenzene, which is a less common substrate in undergraduate chemistry courses. PhOCF3 exhibits directing effects and reactivity in various electrophilic aromatic substitution (EAS) reactions, with a reactivity of around 3-10% compared to benzene. Nobel Laureate Prof. George A. Olah's work on EAS reactions explores the formation of arenium ions, also known as s-complexes or Wheland intermediates, which are crucial in understanding the mechanisms of these reactions. The isolation and characterization of stable intermediate ions from alkylation, nitration, and protonation reactions were described by Prof. Olah's group. A comprehensive review on directive effects in EAS was published by Leon M. Stock and Herbert C. Brown. Additionally, papers by Prof. George A. Olah and his colleagues discuss the characterization of benzenium ions and their role as intermediates in EAS reactions.