Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material: Discussion of Product Yields

The concept of substitution effects indicates a comparably stronger influence of the chlorine substituent on the course of an electrophilic aromatic substitution reaction. In Fig. 5 of the article the product yields of the nitration of the all different monochlorotoluenes are exemplified. Before discussing the quadrupole coupling and reactivity we take a closer look to the concept of substitution effects. Both substituents, chlorine and methyl, are classified as electron pushing relative to the phenyl ring with their +M and +I effects, respectively. In the case of chlorine, this leads to a partial negative charge in *ortho*- and *para*-position.

For a methyl substituent the interaction, characterised by hyperconjugation, some charge aggregation is expected just in its *ortho*-positions. This, together with steric effects, leads to a preference of the chlorine's *para*-position as target for an electrophilic aromatic substitution. Also the case exemplified by *m*-chlorotoluene provides compelling evidence that such concepts of directing substituents indeed work. The main product **6** satisfies both conditions with the nitro group introduced in *para* and *ortho*-positions of the chlorine and methyl substituents, respectively. A direct comparison of **6** with the product **8** indicates the influence of the methyl group: While both positions are favoured by the substituents (*para* and this *ortho* position are electronically and sterically quite similar), only in **6** the nitro group is introduced next to the methyl group and its +I effect. The latter leading to a significantly preferred formation. For the *ortho*, *ortho* product **5** on the other hand, steric screening reduces the formation significantly. For *p*-chlorotoluene, somewhat surprisingly, the main product **9** indicates a more pronounced directing effect of the methyl substituent. Nevertheless, the yield ratio of **4**, *ortho* to chloro (electron pushing) and *meta* to methyl (no influence), to **1**, *meta* to chloro and *ortho* to methyl, of 0,908 was already indicating the now more pronounced ratio of the equivalently substituted *p*-halotoluene products **10** and **9** of 0,724. This might be rationalized with a higher amount of π-bonding character of the chlorine carbon bond in the *ortho*-species, even though it contradicts the empirical rule that the mesomeric effect of a substituent is always stronger than the I effect of an alkyl group. The experimental results indeed support the prediction of an increased π bond character, that the concept delivers explaining the observed yields. This obviously does not mean, that the substitution effects concept reflects the underlying molecular physics directly. For a more detailed insight a variety of quantum chemical calculation methods is nowadays available, but even then, the interplay of experiment and theory is crucial while quantum chemical predictions also need benchmarks and validation by experiments to prove predictive power and trustworthiness.