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ELECTROPHILIC SUBSTITUTION OF AMINOPHENOLS AND AMINOBENZENETHIOLS BY TRIPHENYLMETHYL CARBONIUM ION

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Abstract—The electrophilic substitution of aminophenols and aminobenzenethiols by trityl cation has been studied. The *ortho*- and *meta*-aminophenol are substituted in the position "*para*" to the amino group, while the *para*-aminophenol does not react at all, and the aminobenzenethiols are all substituted at the SH-group. MO calculations have been carried out in order to predict the position of attack. Electron densities, free valences and cation localization energies do not give the right prediction, but the ion free valence predicts correctly the position of attack. This observation allows conclusion about the nature of the transition state of the reaction. The substitution of the aminobenzenethiols at the thiol group can be explained on the basis of electron promotion to the 3d orbital. Assuming 3d expansion the maximum bond order N_{max} of sulfur has been calculated as 1·664.

INTRODUCTION

TRITYLATION of aminophenols and aminobenzenethiols have been recently described by Chuchani *et al.*[1,2] The results showed that the point of attack in the aminophenols is always "*para*" to the amine substituent, whereas in the aminobenzenethiols attack takes place at the S atom. Although some physical constant such as the pK_a values of benzenethiols when compared with the pK_a values of phenols[3-5] imply a greater delocalization of the *p*-electrons of sulphur with the Π-system and activation of the ring, the tritylation results are not in contradiction with the lack of activation of the SH group on the aromatic nucleus with inorganic electrophiles. A number of examples are known in which an electrophile attacks at the sulfur and not at the benzene ring.[6-8] An interesting fact related to this phenomena is that the mesomeric moment of benzenethiol compared with phenol, indicates lesser conjugation between sulfur and the ring than between the oxygen and the ring.[9]

The present work has been undertaken in order to show if the reason for electrophilic attack at the S atom is due to *d*-orbital participation. Therefore, we have carried out some MO calculations on these compounds.

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Molecular orbital calculations

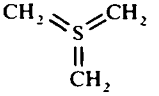
Huckel MO calculations were carried out in the well established manner.[10]

For the heteroatoms the following parameters have been used:

$$h_{\ddot{O}} = 2{\cdot}0; \quad k_{C-OH} = 0{\cdot}9$$
$$h_{\ddot{N}} = 1{\cdot}5; \quad k_{C-NH_2} = 0{\cdot}9$$
$$h_{\ddot{S}} = 1{\cdot}0; \quad k_{C-SH} = 0{\cdot}8$$

All α-carbons have been assigned a $h_{C\alpha} = 0{\cdot}1$.

The h-values are usually chosen according to the electronegativity of the atom. Pauling's electronegativity scale[10] would therefore indicate an h-value for sulfur of 0·0 (equal to carbon), but the sulfur in our case contributes two Π-electrons to the system, and the α should therefore be considerably more negative than the α for carbon, which contributes only one Π-electron. This important distinction has been first pointed out by Streitwieser,[11, 12] who determined the difference $h_{\ddot{X}} - h_{\dot{X}}$ to be about 1·0–1·5. A value for $h_{\ddot{S}} = 1{\cdot}0$ appears therefore to be reasonable. The values for oxygen have been successfully used by Pullman.[13a] If $h_O = 2{\cdot}0$ and $h_S = 1{\cdot}0$ h_N has to be taken as 1·5 according to Pauling's electronegativity scale. The results of the calculations using the above parameters are summarized in Table 1. The parameter values for oxygen and nitrogen have been successfully used in literature,[10] but in order to obtain some confidence in the sulfur parameters, we have used the following combinations of parameters for $h_{\ddot{S}}$ and k_{C-SH} resp: (1·0/0·8), (1·0/1·0), (1·3/1·0), (1·5/1·0), (1·8/1·0), (1·5/0·8), (1·0/0·6), (0·0/0·8), (0·0/1·0). In all of these calculations we find that the reactivity indices (q_r, F_r and F_r^+) at the sulfur are always smaller than the reactivity indices at the oxygen in the corresponding aminophenols, assuming no valence shell expansion of the sulfur (i.e. N_{max} for oxygen = N_{max} for sulfur = 1·0).[13b] Free valence on sulfur has not been defined in the literature. We have therefore calculated the maximum bond order (N_{max}) of sulfur assuming 3d orbital participation. The bond in trimethylene sulfur I has been calculated.*



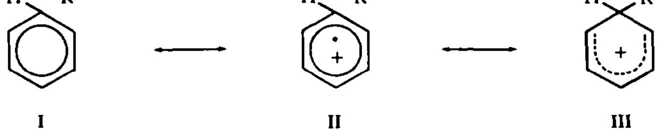
I

Using $h_{\ddot{S}} = 1{\cdot}0$ and $k_{C-S} = 1{\cdot}0$ the bond order in I is 0·5547 or N_{max} of sulfur 1·664.

If no valence shell expansion occurs then sulfur would be expected to have about the same N_{max} as oxygen. The free valences in Table 1 are all calculated assuming no valence shell expansion (N_{max} of oxygen = N_{max} of sulfur = 1·0).

DISCUSSION

The transition state of electrophilic aromatic substitution may be represented by a reasonable hybrid of the following structures (I–III):



I II III

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* We acknowledge the useful comments of the referee concerning N_{max}.

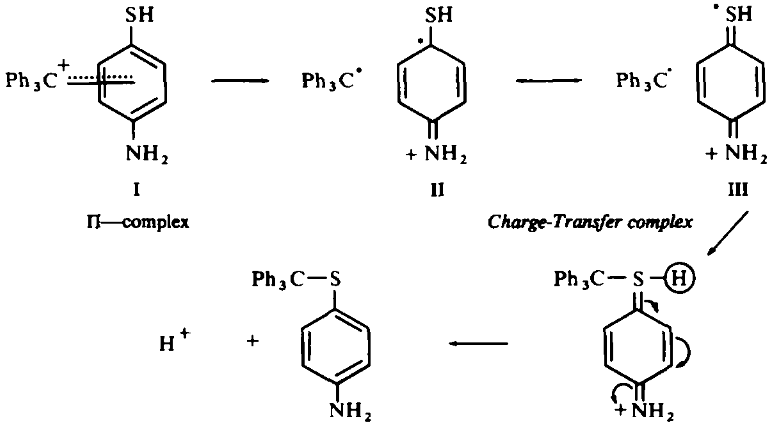
Depending on which structure (I, II or III) resembles more closely the transition state different reactivity indices will have to be considered. In structure I the Π-system is little disturbed and the reactivity will be determined by the electron density (q_r) or free valence (F_r) in the parent compound. Structure II is the charge transfer structure and the tendency for reaction will be determined by the frontier electron density[14] or by the free valence in the radical ion.[15] Finally for structure III the cation localization energy[16] will be the appropriate reactivity index to consider.

The results in Table show that only the ion free valence (F_r^+) correctly predicts the point of attack by triphenylmethyl carbonium ion. The *ortho*- and *meta*-aminophenol react "*para*" to the amino group, whereas *para*-aminophenol does not react at all. The ion free valence in the *ortho*-positions of the *para*-aminophenol is considerably lower (0·455 and 0·483 resp.) than F_r^+ in *ortho*-and *meta*-aminophenol at the position "*para*" to the amino group (0·512 and 0·616 resp). For substitution on carbon a minimum ion free valence of about 0·5 appears to be required. Another example in which a minimum free valence is required for homolytic aromatic substitution by a resonance stabilized radical is the reaction of benzyl radical with aromatic hydrocarbons.

Benzyl radicals do not react with benzene ($F_r = 0{\cdot}399$), naphthalene (maximum $F_r = 0{\cdot}453$), and pyrene (maximum $F_r = 0{\cdot}468$), but react with anthracene (maximum $F_r = 0{\cdot}520$).[17]

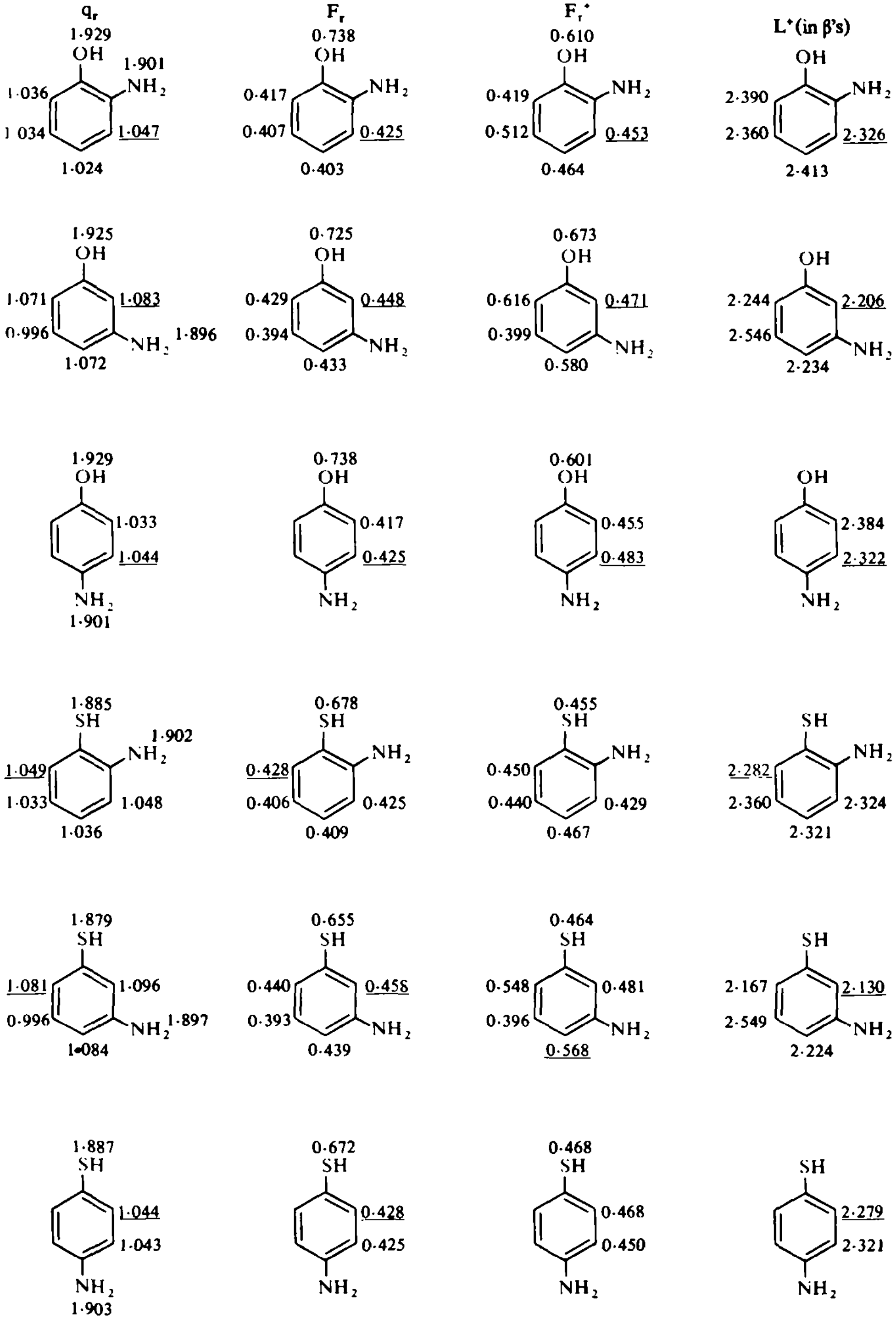
If we compare F_r^+ values in the *p*-aminophenol and *p*-aminobenzenethiol we see that *p*-aminobenzenethiol should not react at the *ortho*-positions because the ion free valence is lower than 0·5, and it should not react at the sulfur because F_r^+ is lower than at the oxygen in the *p*-aminophenol. The only way to rationalize the experimental fact is to assume valence shell expansion on sulfur, which would considerably increase the ion free valence at the sulfur (from 0·468 in *p*-aminobenzenethiol to 1·132).

The tritylation reaction may be represented by the following sequence:



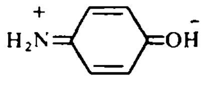
For the structure of the charge transfer complex II we can also write a resonance structure III in which the unpair of *p*-electrons is localized at the S atom expanding its

TABLE 1. REACTIVITY INDICES IN AMINOPHENOLS AND AMINOTHIOPHENOLS. THE UNDERLINED NUMBERS REPRESENT THE PREDICTED POINT OF ATTACK BY AN ELECTROPHILE

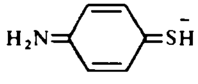


valence shell. The formation of σ-bonds between the trityl species* and the radical ion takes place at the sulfur because of the important contribution of structure III to the resonance hybrid. On the other hand, in the aminophenols structure like III cannot contribute to the resonance hybrid of the transition state, because no valence shell expansion is possible at the oxygen atom. Reaction occurs instead at the benzene ring.

In a recent paper[5] σ_R-values for aminophenols and aminobenzenethiols have been reported. These parameters were obtained from pK_a measurements and were found to be nearly identical in the two types of compounds. In the case of *p*-aminophenol, the decrease in acidity as compared with phenol has been explained on the basis of resonance structure IV



IV



V

This rationalization however suggests valence shell expansion at the oxygen, which is not known to occur. On the other hand, this type of resonance interactions appears to be reasonably in *p*-aminobenzenethiol (V) since sulfur is capable of expanding its valence shell. The similarity of σ_R-values for aminophenols and aminobenzenethiols indicate no such difference between the two types of compounds. The valence shell expansion in the tritylation of aminobenzenethiols is therefore dependent on the approaching electrophile, i.e., the formation of the charge transfer complex II⟷III.

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[*] The trityl species is not a free radical. The structure II⟷III serves only as a model for the Molecular Orbital Calculations.