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THE USE OF MOLECULAR ELECTROSTATIC POTENTIALS IN THE STUDY OF THE PROTONATION OF TOLUENE

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Abstract—The protonation of toluene has been studied using electrostatic potential plots. A basic assumption is that at the start of the reaction the aromatic hydrogen atom moves out of the plane of the ring forming a tetrahedral carbon. When the charges on the ortho, meta or para centres are considered alone ortho attack is predicted, whereas consideration of the potential due to the sum of the nuclear and electronic charges permits the interpretation of the preferred para-protonation of toluene.

Olah *et al.*[1] have shown by NMR that toluene protonates in the para position when dissolved in supraacid at −97°C. When the reaction takes place at the most highly charged atom, it is said to be charge-controlled;[2] when the reaction takes place at the atom with the highest frontier orbital electron density it is said to be frontier orbital controlled. The total charge on the ortho carbon of toluene (4.012) is greater than that on the para carbon (4.005) (CNDO/2 calculation). On the contrary the frontier orbital coefficient is greater for para (0.530) than ortho (0.319). Therefore the para protonation of toluene would seem to be frontier orbital controlled. Charge controlled reactions have been identified by Klopman[2] with the hard acid/hard base interactions of Pearson's classification[3] and frontier orbital controlled reactions with those of the soft acid/soft base type. Accordingly the proton should be a soft acid, in fact it is classed among the hard acids due to its small size and consequent very high charged density.[3] The simplistic interpretation of the protonation of toluene therefore fails. Politzer and Weinstein[4] have also recently shown that a simple consideration of the charges on the ring carbons of heterocyclic species does not account for the latter's reactivity towards electrophiles.

Bonaccorsi *et al.*[5] have proposed a treatment in which the nuclear and electronic charges give rise to a potentiel in the space surrounding the molecule. Since this potential is an observable, in the quantum mechanical sense, this approach is particularly useful as it represents a better model of the system as seen from the approaching reactant. The energy of interaction of a charge q with this potential field is qV. A plot of the isopotentials obtained in this way give the energy of interaction of an isolated proton and they enable one to predict the point of attack of various electrophiles.[6] It has often been shown that refinements such as polarization effects, charge transfer and optimization of the molecular geometry do not modify the results predicted by the electrostatic model.[7] The following study of the protonation of toluene is therefore based on this model.

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The potentials were calculated using the CNDO approximation. In Fig. 1 the curves are plotted for a plane parallel to and 2.2 Å from the ring. They represent the repulsive field experienced by a point positive charge, and it can be seen that the further away from the methyl group, the lower is the repulsion. At large distances the polarization and charge-transfer are small and the variation of energy with the angle of attack becomes essentially that of the electrostatic interaction between the substrate and an approaching species. The repulsive potentials being lower around the para position than around the ortho, para attack will be favoured over ortho.

We have also used the idea developed by Politzer and Weinstein[4] in their study of the electrophilic attack on furan, by plotting the isopotentials where successively the ortho (Fig. 2a), meta (Fig. 2b) and para (Fig. 2c) hydrogen have been move out of the plane of the ring. The angle between the C–H bond and the plane of the ring has been set at 50°45′ which is the optimum angle for tetrahedral

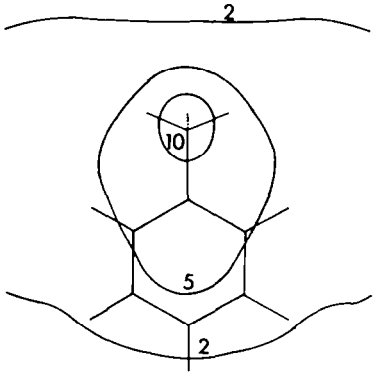

Fig. 1. Electrostatic potentials (in kcal/mole) in a plane 2.2 Å above the ring-plane of toluene.

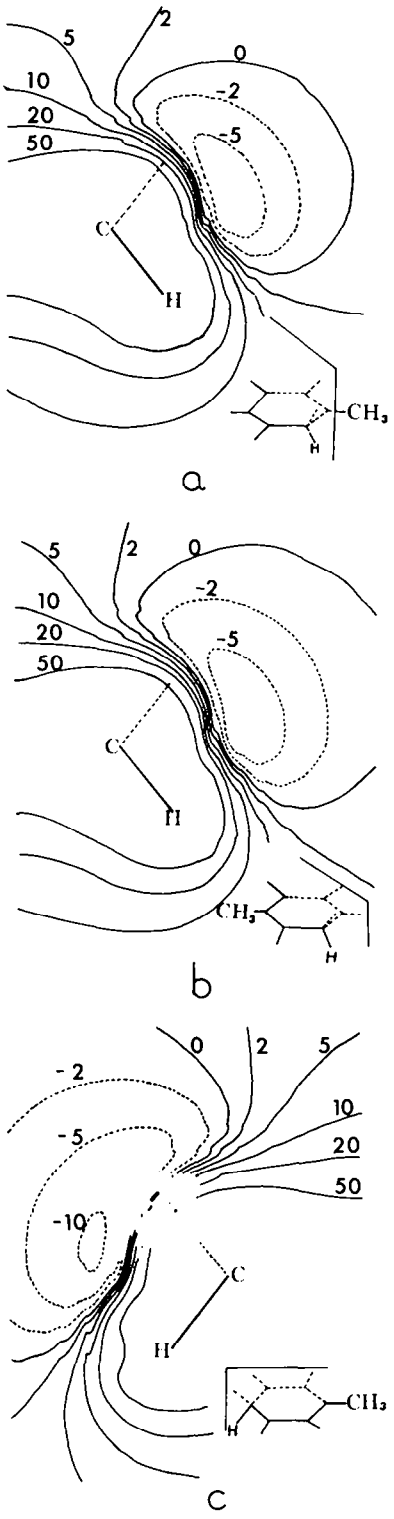

Fig. 2. Electrostatic potentials (in kcal/mole) at right angles to the plane of the ring (negative potentials—dotted lines) with (a) ortho, (b) meta, (c) para hydrogens moved out of the plane of the ring.

hybridisation without deformation of the ring. In the three cases attractive potentials approximately centring on the direction of the vacant tetrahedral position are obtained, the highest being at the para position. Thus, although the charge on the para carbon (4.070) is lower than that of the ortho (4.076) the attractive potential turns out to be

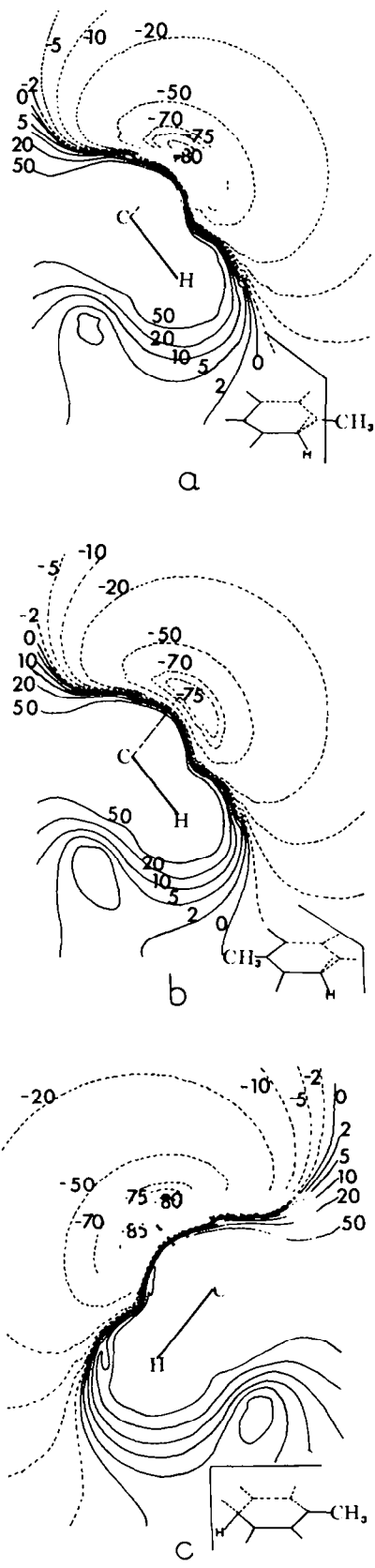

Fig. 3. Toluene is polarized by the proton. Electrostatic potentials (in kcal/mole) in a plane perpendicular to the ring with hydrogens (a) 2, (b) 3, (c) 4 moved out of the plane of the ring (negative potentials—dotted lines).

greater at the para carbon. It should be noted that the change in the charge at the three carbons is very small on deforming the toluene ring.

Up to now the polarization due to the positive charge (H^+) has been ignored. In fact, when taken into account the polarization changes the distribution of the potential. We have considered the case of maximum polarization in which the proton occupies the fourth position of the pseudotetrahedral carbon. Figure 3(a-c) show the isopotentials obtained when the carbons 2, 3 and 4 respectively are tetrahedral. For the calculations of the potentials the β integrals in the SCF matrix were set to zero (i.e. no charge-transfer between the proton and toluene).

The results presented in Fig. 3 show that the attractive potentials have been increased but they do not modify the over all conclusions, viz. that the attractive potential at the para position is the greatest. As in the non-polarized treatment the maximum potential at ortho (−80 kcal/mole) is less than at para (−85 kcal/mole) whereas the charges they carry are in the inverse order (ortho 4.579, para 4.574).

CONCLUSION

The classic concept of charge-control in electrophilic addition fails to explain the observed para selectivity in the protonation of toluene. It is necessary to take into account the electrostatic potential created by all electronic and nuclear charges. This preliminary model indicates that electrostatic repulsion is less at the para carbon. On moving the hydrogen atom out of the plane of the ring, attractive potentials appear which are strongest at the para position. This conclusion remains unmodified even under maximal polarization of molecule, the order of the attractive potentials remaining the inverse of the charges carried by the para and ortho carbons.

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