

A THEORETICAL STUDY OF THE EFFECT OF  
SOLVATION BY TRIFLUOROACETIC ACID UPON THE  
ELECTROPHILIC SUBSTITUTION OF TOLUENE

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Molecular orbital theory has been generally successful in correctly predicting the position of electrophilic aromatic substitution.<sup>2</sup> Most of the theoretical predictions agree qualitatively with partial rate factors and/or the most stable ion resulting from protonation in superacids. It has been claimed that the relative energies of cationic species in superacids closely parallels their gas phase energies.<sup>3</sup>

Nevertheless there are quantitative and even qualitative differences between superacid experiments and typical partial rate factors for electrophilic substitution. This paper deals with a theoretical approach to treating the specific solvation of protonated aryls by trifluoroacetic acid (TFA) which may explain some of the differences.

Treatment of toluene with magic acid produces a solution whose nmr spectrum is that of only para-protonated toluene<sup>4</sup>. On the other hand, deuteration of toluene with  $CF_3COOD$ <sup>5</sup> or protodeuteration of tritiated toluenes with  $CF_3COOH$ <sup>6</sup> result roughly in 50% reactivity at the ortho positions. One plausible explanation for these observations is that trifluoroacetic acid (TFA) solvates the ortho relatively better than the para protonated toluene. Since theoretical treatments of the interaction of TFA with various carbocations, including the benzenium ion, seems to offer reasonable, if as yet unproven, explanations for solvolytic reactivity in that solvent<sup>7</sup>, we have applied the same solvent-solute model, I, in an attempt to test this explanation.

Molecular orbital calculations at the INDO level were performed individually on ortho, meta, and para-protonated toluene and TFA. Since protonated toluene and 2 TFA's contain 95 basis orbitals at this level, it was considered too expensive to optimize a solvent-solute complex at a more




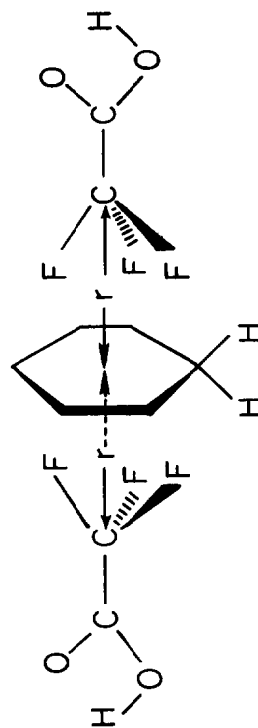
| Geometry  | No TPA                      |               | 1 TPA                       |               | 2 TPA                       |               | experimental %<br>70° -60°         |
|---|-----------------------------|---------------|-----------------------------|---------------|-----------------------------|---------------|------------------------------------|
|   | relative Energy (kcal/mole) | % at 70° -60° | relative energy (kcal/mole) | % at 70° -60° | relative energy (kcal/mole) | % at 70° -60° |                                    |
|  | 2.4                         | 5.7           | 1.1                         | 28.7          | 0.6                         | 45.5          | 54 <sup>a</sup><br>49 <sup>b</sup> |
| optimized   | 2.4                         | 0.07          | 1.1                         | 13.1          | 0.6                         | 32.8          | 0 <sup>c</sup>                     |
| standard <sup>9</sup>   | 2.1                         | 0.14          | 1.3                         | 8.6           | 0.9                         | 19.5          |                                    |
|  | 11.3                        | 0.0           | 14.0                        | 0.0           | 11.6                        | 0.0           | 1 <sup>a</sup><br>1 <sup>b</sup>   |
| optimized   | 11.3                        | 0.0           | 14.0                        | 0.0           | 11.6                        | 0.0           | 0 <sup>c</sup>                     |
| standard <sup>9</sup>   | 9.0                         | 0.0           | 5.8                         | 0.0           | 2.6                         | 3.0           | 0.04                               |
|  | 0                           | 94.3          | 0                           | 71.3          | 0                           | 54.5          | 45 <sup>a</sup><br>50 <sup>b</sup> |
| optimized   | 0                           | 94.3          | 0                           | 86.9          | 0                           | 77.2          | 100 <sup>c</sup>                   |
| standard <sup>9</sup>   | 0                           | 92.8          | 0                           | 91.4          | 0                           | 80.5          |                                    |

Table I Calculated Relative Energies

Percent reaction is calculated by using the relative energies in a Boltzmann distribution (entropy is neglected). The temperatures indicated are those of the hydrogen exchange reactions and nmr experiments respectively.

a) deuteration<sup>5</sup> b) protodetrifiation<sup>6</sup> c) nmr in superacid<sup>4</sup>



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sophisticated level of calculation. For each case the geometry was optimized by a gradient procedure. Optimization was deemed complete when a) two successive calculations differed by less than 0.06 kcal/mole, b) the first derivatives of the energy with respect to independent geometric coordinates were all very small, and c) the second derivatives with respect to these coordinates were all positive. A more detailed discussion of the optimization procedure will appear elsewhere<sup>8</sup>. For toluene and the protonated species, the ring carbons and the atoms directly attached to these carbons (except for the two hydrogens at the protonated carbon) were taken to be coplanar.

Carbon-carbon bond lengths, all bond angles and the dihedral angles involving the hydrogens on the protonated carbon were individually considered in the optimization. The C-H bonds were fixed at their "standard"<sup>9</sup> values. The methyl group was kept eclipsed with respect to aromatic ring to preserve a plane of symmetry in the solvated ions (see below). The geometry of TFA was completely optimized. The energies of the solvated cations were calculated by approaching TFA molecules to the rings as described in figure I. The C-C bond axes of the TFA's were aligned with the center of the aromatic ring. Only the distances between the carbon of the trifluoromethyl group and the center of the ring (held to be equivalent), were optimized. The individual species were held fixed in their previously optimized geometries. Optimized values of  $r$  are 2.30, 2.28 and 2.30 for the ortho, meta and para complexes respectively. Similar calculations were performed using only one TFA, with corresponding values of  $r$  equal to 2.25, 2.24 and 2.26. For comparison purposes, the same calculations were repeated using "standard"<sup>9</sup> geometries for the individual species while only optimizing the distances between the protonated toluene and the TFA's. The calculated energies are collected in Table I.

The agreement between experiment and calculation is almost embarrassingly good for the optimized species and also quite good for the calculations using standard geometries. In both cases  $E_{\text{para}} - E_{\text{ortho}}$  significantly decreased upon solvation while  $E_{\text{para}} - E_{\text{meta}}$  remained large. The theoretical percent ortho/para/meta were obtained using the calculated differences in  $E$ 's in a Boltzmann distribution at the temperatures of the hydrogen exchange experiments (70°C) and the nmr spectra (-60°C). These results definitely support the idea that relative cationic solvation might be quite important in consideration of normal organic reactivities, even if it is relatively unimportant in superacid solution. The quality of the correlation also increases our confidence in the previously suggested<sup>7</sup> model for cation stabilization by TFA.

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