

AROMATIC DETRITIATION VII.<sup>1</sup> A QUANTITATIVE CORRELATION BETWEEN HYDROGEN EXCHANGE RATES AND CHARGE DISTRIBUTION IN THE BENZENONIUM ION.

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Some years ago MacLean *et al.* showed that the positive charge distribution in the penta- or hexamethylbenzenonium ion was ortho, 0.215; meta, 0.16; and para, 0.25,<sup>2</sup> and this is qualitatively compatible with the positional electrophilic reactivity of aromatics containing electron-supplying substituents in reactions with transition states resembling the Wheland intermediate *viz.*  $p > o > m$  (and vice versa for those containing electron-withdrawing substituents).<sup>3</sup> The numerical value for the charge for the meta-position was however somewhat dependent upon the reference point chosen for measuring the chemical shifts in the n.m.r. method employed and a more recent investigation of the chemical shifts in the benzenonium ion itself indicates the charge densities to be as in Fig. 1.<sup>4</sup> These values are in very good agreement with those calculated theoretically by MacLean *et al.*<sup>2</sup> using the method of

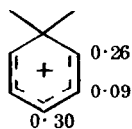


Fig. 1.

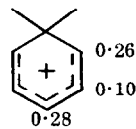


Fig. 2.

Wheland and Mann<sup>5</sup> (Fig. 2).

We now report that the values shown in Fig. 1. are not merely qualitatively in accord with experimental reaction rates, but for hydrogen exchange quantitative agreement is obtained. The values in Fig. 1. are believed to be a composite of  $\pi$ - and  $\sigma$ -electron densities,<sup>2</sup> and consequently correlation should be obtained with substituents where the electronic effects either act in the same direction or where

one effect is very dominant, and in a reaction where the demand for resonance is large i.e. the transition state is well on the way to the Wheland intermediate. Hydrogen exchange is just such a reaction and moreover, steric effects are usually absent. We recently drew attention to the fact that the  $\log \frac{f_o}{f_p} / \log \frac{f_m}{f_p}$  ratios for detritiation (in trifluoroacetic acid) of aromatics containing the Me, Et, CH<sub>2</sub>Ph, OMe, SMe, OPh, and SPh substituents were remarkably similar ( $0.865 \pm 0.05$ ).<sup>6</sup> It is now seen that this is precisely the value predicted from the data in Fig. 1. (and also from the original data of MacLean et al.) To these values we can now add our unpublished data for the (CH<sub>2</sub>)<sub>2</sub>Ph (0.83) and cyclopentyl (0.89) substituents and in addition, data is available for *t*-butylbenzene (0.875),<sup>7</sup> 4'-trimethylsilylbutylbenzene (0.865)<sup>8</sup> biphenyl (0.90)<sup>9</sup> and fluorene (0.88).<sup>10</sup> It is clear then that for these aromatics a linear free energy relationship exists between the reactivities at the ortho and para positions, and we note that the existence of such a correlation was forecast by Eaborn et al.<sup>11</sup>

This correlation is not limited merely to hydrogen exchange though for other reactions there are the complications referred to above. Nevertheless, for the methoxy substituent, the ratios are available in molecular bromination (0.805),<sup>12</sup> molecular chlorination (0.885),<sup>13</sup> protodesilylation (0.795),<sup>14</sup> and protodegermylation (0.84),<sup>15</sup> the agreement being quite remarkable. Data too are available for the methyl substituent though because it is less electron supplying, the dominance of inductive (or field) effects (which can seriously affect ortho reactivities) lead one to anticipate less precise correlations here. Omitting those reactions for which steric hindrance and these ortho facilitation mechanisms may be severe we have 0.76 (bromination in trifluoroacetic acid or sulphur dioxide)<sup>16, 17</sup> 0.86 (chlorination in acetonitrile),<sup>16</sup> 0.91 (nitration, iodination)<sup>16, 18</sup> and 0.95 (protodesilylation, protodegermylation, and chlorination in acetic acid),<sup>14-16</sup> agreement here is also good considering the other variables that probably apply.

It follows from the above that strongly deactivating substituents should give the same ratio. Unfortunately for hydrogen exchange no data are available and indeed little can be obtained from the published literature on other reactions. We note, however, that the NO<sub>2</sub> substituent in nitration gives 0.86,<sup>19</sup> and the SO<sub>3</sub>H (probably SO<sub>3</sub><sup>-</sup>)<sup>20</sup> and CO<sub>2</sub>H substituents give 0.825 and 0.88 respectively in protodesilylation.<sup>14, 21</sup>

Finally the charge distribution predicts a  $\log \frac{f_p}{f_m} / \log \frac{f_m}{f_o}$  ratio of 3.3. Results are limited in hydrogen exchange to the methyl substituent, and it is satisfying to note that reliable partial rate factors give the

values of 2.9 - 3.4 in very good agreement<sup>22</sup> and similar values are obtained in a wide range of other electrophilic substitutions.

It follows from the above of course that under favourable conditions it is possible to apply  $\sigma_{\text{ortho}}^+$  values to certain substituents and in certain reactions. The restrictive conditions are rather severe, consequently the predictive value of these parameters is limited. Nevertheless it appears feasible at this time to propose values of -0.67 (o-MeO), -0.515 (o-MeS), -0.455 (o-PhO), -0.405 (o-PhS), -0.27 (o-Me), -0.225 (o-t-Bu), and -0.155 (o-Ph).

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