A micro-analysis of the helium and neon contents of air


The structure and reactivity of the halogenobenzenes

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The structure of the halogenobenzenes is described in terms of an inductive effect acting on the meta-positions and polarization between neighbouring atoms, in addition to the well-recognized mesomeric and inductive effects at the ortho- and para-positions. Data on the side-chain reactions of aromatic compounds are correlated with those on nitration (with recognition of the effect of transition-state resonance in the latter case) to provide estimates of the charge distribution in the aromatic nucleus. The dipole moments of the halogenobenzenes are calculated.

The present theory of the structure and substitution of aromatic molecules, due to Lapworth, Robinson, Ingold and others, which has proved so successful qualitatively, appears to be ready for quantitative extension. An attempt to provide a starting point for the discussion of the case of the halogenobenzenes is described below.

The slow substitution, compared with benzene, of these compounds in the ortho- and para-positions has been explained in terms of an inductive effect (I) and a mesomeric effect (II) of the electronegative substituent (X).
Whilst the order F < Cl < Br < I has been suggested for the strength of the mesomeric effect (Ingold 1934; Hugill, Coop & Sutton 1938), Baddeley & Bennett (1933) concluded from their studies of side-chain reactions that the opposite is true, as did Groves & Sugden (1937) from their work on dipole moments. Of all aromatic molecules considered the halogenobenzenes were treated least satisfactorily by quantum-mechanical methods embodying the above ideas (Wheland & Pauling 1935). Although Ri & Eyring (1940) achieved greater success by adopting the semi-empirical procedure of comparing the observed dipole moments with those calculated from the rates of nitrination, the divergences from experiment are sufficiently great to require a reconsideration of the problem ab initio.

The mesomeric effect is the result of the contribution of states III, IV and V to the resonance hybrid:

![Resonance Hybrid Diagram]

Ri & Eyring's simplification of assuming that the participations of all these are equal, is acceptable for the purpose of rough calculations. Their division of the positive charge equally between the halogen and the carbon atom to which it is attached (C₁) was not explained, and in the following calculations it is placed entirely on the halogen itself, as in the above formulae. Inspection will show, however, that this change does not affect the results obtained by the revised method employed here.

The inductive effect has been described as resulting in general deactivation of the whole nucleus (Ingold 1933). On the ground that the benzene nucleus acts as a conductor of charge, Ri & Eyring (1940) made the more definite assumption that equal charges are removed from all six carbon atoms and are balanced by an opposite charge on the halogen: it was not explained why the charge from the mesomeric effect should not be similarly distributed, justification in a further publication being promised. On the other hand, Wheland & Pauling (1935) considered that the ortho- and para-positions received the main inductive charge. Now the electronegative nature of the halogen expresses itself in the ionic character of the carbon-halogen bond. The positive charge on C₁, arising from this polarity, will be transmitted to the meta-positions by the conjugated aromatic system, so that the resonance states VI, VII and VIII are to be regarded as a source of the inductive effect:

![Inductive Effect Diagram]
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The proportion of the charge actually carried by the meta-positions will depend on the degree of disturbance of the electronic orbitals of the benzene nucleus by the halogen ion, and on the strain between the double bonds in forms VII and VIII. The importance of these factors cannot be estimated readily at present. Another mechanism of action of the inductive effect is already well recognized, namely that the electron deficiency on C₁ may be partially satisfied by the contribution of the resonance states IX, X and XI:

\[
\begin{align*}
&\text{IX} & & \text{X} & & \text{XI} \\
\end{align*}
\]

The quantitative correlation of the dissociation constants of the fatty acids (Derick 1911; Branch & Calvin 1941) has led to the conclusion that a charge on one carbon atom produces a like charge, or polarization, of one-third its magnitude on immediately neighbouring atoms, and that such charges are additive, provided that saturation is not approached. In the following calculations this result is applied to the benzene nucleus, without making any special allowance for the influence of double bonding on the magnitude of the effect. The introduction of ‘polarization’ to specify what is generally described as ‘induction’ in aliphatic compounds is necessitated by the common usage of the latter term for the resonance phenomena already mentioned.

Following now Ri & Eyring, the validity of the above ideas may be conveniently tested by comparison of the observed dipole moments with those calculated. The charge distribution is defined by equations (1)–(5):

\[
\begin{align*}
e_p &= e_p^a + e_p^b + \frac{2}{3} e_m^b, \\
e_m &= e_m^b + \frac{1}{3} (e_p^a + e_p^b) + \frac{1}{3} (e_0^a + e_0^b), \\
e_0 &= e_0^a + e_0^b + \frac{1}{3} (e_m^a + e_1^a), \\
e_1 &= e_1^a + e_1^b + \frac{1}{3} (e_0^a + e_0^b), \\
e_x &= -(e_1^a + 2e_0^a + 2e_m^a + e_p^a),
\end{align*}
\]

where \(e_y\) specifies the charge on the atom \(y\) relative to that in benzene, the superscript \(a\) specifies the charge from the mesomeric effect (resonance states III–V), the superscript \(b\) specifies the charge from the inductive effect (resonance states VI–VIII), the superscript \(c\) specifies the charge from the inductive effect (resonance states IX–XI). Polarization is regarded as simply modifying the charge distribution produced by the mesomeric and inductive effects, whilst the disturbance of distant atoms and more subtle readjustments of charge are ignored. Any polarization of \(C_1\)
by $X$ is included in the inductive charge on $C_1$. Other approximate treatments based on the same principles are possible and yield similar results.

Substitution of the simplifications that $e_0^a = e_p^a$ and that $e_0^b = e_p^b$ yields the following relations:

$$e_p^{(a+c)} = \frac{3}{8}e_p - \frac{6}{5}e_m,$$

$$e_m^{(a+c)} = \frac{3}{8}e_m - \frac{6}{5}e_p,$$

$$e_1^{(a+c)} = e_1 - \frac{3}{8}e_p^{(a+c)},$$

$$e_1 = 3e_0 - 3e_p + e_m,$$

$$e_X = 2e_p - 5e_0 - 3e_m,$$

whilst

$$\mu = e_X (r_x + r_b) + r_b (e_1 + e_0 - e_m - e_p),$$

where $r_X$ is the $C_1-X$ distance, $r_b$ is the C–C distance, $\mu$ is the dipole moment.

It remains to determine the values of $e_0$, $e_m$ and $e_p$. Ri & Eyring (1940) assumed that an increase on substitution of benzene in the velocity constant of nitration ($k_y$) is caused by lowering of the free energy of activation ($\Delta F^+$) by the energy of electrostatic interaction in the transition state between the charge of the reagent, NO$_2^+$, ($e_m$), and that relative to benzene of the substituted carbon atom, ($e_y$). This is expressed according to the theory of absolute reaction rates by equation (6):

$$k_y = K \frac{kT}{h} \exp \left[ - \left( \frac{\Delta F^+ + e_y e_m}{rD} \right) / kT \right],$$

where $K$ is the transmission coefficient, $r$ the distance between the carbon atom and the reagent, and $D$ the effective dielectric constant of the medium. Equation (6) may be put in the form

$$\log \frac{k}{k_0} = - \frac{e_y e_m}{2.303rDkT},$$

where $k_0$ is the reaction constant for benzene itself. Insertion of the numerical values gives the result

$$\log \frac{k}{k_0} = - 32.5 e_y$$

(all values of $e$ quoted are in $10^{-10}$ e.s.u.).

Hammett (1937, 1940), from experiments on the reactions in the side-chain of meta- and para-substituted aromatic compounds, derived values of a substitution constant, which he considered to be a measure of the electric charge at the point of attachment of the side-chain to the benzene nucleus. The substitution constant, $\sigma$, is related to the velocity or equilibrium constant of the reaction, $k$, by equation (8), in which $\rho$ is a constant for the reaction (with the value of unity for the ionization of the benzoic acids):

$$\rho \sigma = \log k - \log k_0.$$
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Hammett (1940) also claimed that this expression held approximately for nitration with a value of $\rho$ of about $-5$. Combination of (7) with (8) yields equation (9):

$$
\sigma = -\frac{e_m}{2.303rDkT\rho} e_y.
$$

If $\rho$ is equal to $-5$, then

$$
\sigma = 6.5e_y.
$$

Figure 1, in which the actual values of $\sigma$ and $e$ for the halogenobenzenes and toluene are plotted, shows that the data for meta-substitution fit satisfactorily the line

$$
\sigma = 3.6e.
$$

The discrepancy between this and the previously calculated result implies the selection of a value of $\rho$ other than that proposed by Hammett, who considered the results from the meta- and para-positions indiscriminately.

On the other hand, the reaction constants for the para-position show significant deviations which are given in table 1.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$e_p$ or $e'_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>-0.006</td>
</tr>
<tr>
<td>F</td>
<td>-0.015</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.036</td>
</tr>
<tr>
<td>Br</td>
<td>-0.034</td>
</tr>
<tr>
<td>I</td>
<td>-0.070</td>
</tr>
</tbody>
</table>
The proportion of the charge actually carried by the meta-positions will depend on the degree of disturbance of the electronic orbitals of the benzene nucleus by the halogen ion, and on the strain between the double bonds in forms VII and VIII. The importance of these factors cannot be estimated readily at present. Another mechanism of action of the inductive effect is already well recognized, namely that the electron deficiency on C₁ may be partially satisfied by the contribution of the resonance states IX, X and XI:

![Resonance Structures IX, X, XI](image)

The quantitative correlation of the dissociation constants of the fatty acids (Derick 1911; Branch & Calvin 1941) has led to the conclusion that a charge on one carbon atom produces a like charge, or polarization, of one-third its magnitude on immediately neighbouring atoms, and that such charges are additive, provided that saturation is not approached. In the following calculations this result is applied to the benzene nucleus, without making any special allowance for the influence of double bonding on the magnitude of the effect. The introduction of ‘polarization’ to specify what is generally described as ‘induction’ in aliphatic compounds is necessitated by the common usage of the latter term for the resonance phenomena already mentioned.

Following now Ri & Eyring, the validity of the above ideas may be conveniently tested by comparison of the observed dipole moments with those calculated. The charge distribution is defined by equations (1)–(5):

\[ e_p = e^a_p + e^b_p + \frac{2}{3} e^c_m, \]  
(1)

\[ e_m = e^b_m + \frac{1}{3} (e^a_p + e^c_p) + \frac{1}{3} (e^a_0 + e^c_0), \]  
(2)

\[ e_0 = e^a_0 + e^b_0 + \frac{1}{3} (e^b_m + e^c_1 + e^c_1), \]  
(3)

\[ e_1 = e^b_1 + e^c_1 + \frac{2}{3} (e^a_0 + e^c_0), \]  
(4)

\[ e_x = -(e^b_1 + 2e_0 + 2e_m + e_p), \]  
(5)

where \( e_y \) specifies the charge on the atom \( y \) relative to that in benzene, the superscript \( a \) specifies the charge from the mesomeric effect (resonance states III–V), the superscript \( b \) specifies the charge from the inductive effect (resonance states VI–VIII), the superscript \( c \) specifies the charge from the inductive effect (resonance states IX–XI). Polarization is regarded as simply modifying the charge distribution produced by the mesomeric and inductive effects, whilst the disturbance of distant atoms and more subtle readjustments of charge are ignored. Any polarization of C₁
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further experimental work, it seems legitimate to interpolate the value quoted (0.064).

Values of dipole moments: Audsley & Goss (1942).
Values of bond distances: Ri & Eyring (1940).

Agreement with experiment is as satisfactory as can be expected. The apparent
charges produced by resonance in the transition state during nitration in the ortho-position (F, -0.041; Cl, -0.016; Br, -0.019; I, -0.065) show a similar trend
to those for the para-position, apart from that of fluorine. This anomaly may be
related to the larger charge on, and smaller size of, the fluorine atom. On the other
hand, it is noticeable that the values of $e_p^{(a+c)}$ are in the reverse order, and that of
iodine even positive.

<table>
<thead>
<tr>
<th>$e_0$</th>
<th>$e_m$</th>
<th>$e_p$</th>
<th>$e_m^{(a+c)}$</th>
<th>$e_p^{(a+c)}$</th>
<th>$e_1$</th>
<th>$e_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.077</td>
<td>0.063</td>
<td>0.064</td>
<td>0.084</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.093</td>
<td>0.115</td>
<td>0.116</td>
<td>0.091</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>0.017</td>
<td>0.063</td>
<td>0.065</td>
<td>0.077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>-0.087</td>
<td>-0.025</td>
<td>-0.022</td>
<td>0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.147</td>
<td>0.131</td>
<td>0.131</td>
<td>0.072</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.327</td>
<td>0.132</td>
<td>0.128</td>
<td>0.092</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.273</td>
<td>0.115</td>
<td>0.113</td>
<td>0.112</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.630</td>
<td>-0.534</td>
<td>-0.538</td>
<td>-0.539</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{calc}$ (in D)</td>
<td>-1.43</td>
<td>-1.64</td>
<td>-1.77</td>
<td>-1.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{observed}$</td>
<td>-1.44</td>
<td>-1.64</td>
<td>-1.68</td>
<td>-1.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{mean}$</td>
<td>-1.43</td>
<td>-1.60</td>
<td>-1.72</td>
<td>-1.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{(a+c)}$</td>
<td>-1.20</td>
<td>-1.54</td>
<td>-1.68</td>
<td>-1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{(a+c)}$</td>
<td>-1.09</td>
<td>-1.78</td>
<td>-1.92</td>
<td>-1.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{(a+c)}$</td>
<td>-1.34</td>
<td>-1.62</td>
<td>-1.74</td>
<td>-1.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The question of the carbon-halogen bond distance has not been discussed, since
the effect of ionic type resonance on it is not clear at the moment (Schomaker &
Stevenson 1941; Burawoy 1943; Warhurst 1944). Quantum-mechanical treatments
(Sherman & Ketelaar 1939; Ketelaar 1939) which have been published so far con-
sider only the resonance contribution of states III, IV and V.

The application of these ideas to other series of aromatic compounds is hampered
by lack of suitable data, and by the complexities introduced when the substituent is
polyatomic. However, the degree of success so far achieved in a limited field may be
held to give encouragement for the extension of semi-empirical quantitative methods
to aromatic compounds, including heterocyclic systems, in general. It will be
observed that the complication of additional refinements cannot be tolerated by a
calculation, such as the above, relying on a restricted supply of data (here the
reactivity of the ortho-, meta- and para-positions) without further definition of the
theoretical basis.

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work, and Dr G. Baddeley for helpful discussions.
REFERENCES

Derick 1911 J. Amer. Chem. Soc. 33, 1132.
Ingold 1934 Chim. Rev. 15, 244.
Ketelaar 1939 Rev. Trav. chim. Pays Bas. 43, 266.
Kindler 1927 I bigs Ann. 452, 90.
Kindler 1928 I bigs Ann. 464, 278.
Ri & Eyring 19 J. Chem. Phys. 8, 433.
Sherman & Ketelaar 1939 Physica, 6, 572.
Wheland 1942 Amer. Chem. Soc. 64, 900.