Force Constants in the Hydrogen Halides and Ionic Radii

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Let us make the rather bold assumption that the bond in the hydrogen halides is suddenly disrupted when the hydrogen atom is removed to a certain distance \( r_2 \) from the centre of the halide atom. Outside this limiting distance we then have the bond order 0 while inside we reckon with a bond order 1 \(^1\). We further assume that the interatomic force is quasi-elastic so that the increase in potential energy on moving the proton from the equilibrium distance \( r_1 \) to \( r_2 = r_1 + \Delta \) is approximately \( E = \frac{\Delta}{4C} \) \(^2\) where \( C \) is the force constant. (Outside \( r_2 \) \( C \) is 0). Identifying \( E \) with the dissociation energy \( \varepsilon \) of the molecule (— for dissociation into atoms —) we get approximately

\[
\Delta = \sqrt{\frac{2\varepsilon}{C}}
\]

or when \( \varepsilon \) is in e. v., \( r_1 \) in Å, \( C \) in \( 10^5 \) c. g. s. units and \( \Delta \) in Å:

\[
\Delta = 0.566 \sqrt{\frac{\varepsilon}{C}}
\]

Hence we can easily calculate the "limiting distance" from the halide centre: \( r_2 = r_1 + \Delta \) because \( r_1 \) and \( C \) are known from the infrared spectra \(^1\) and \( \varepsilon \) is also known \(^2\).

It is remarkable that these "limiting distances" come out nearly identical with the van der Waals or ionic radii of the halides as seen from the table below. (As Pauling has shown the ionic and van der Waals radii are nearly identical \(^3\)).

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their radioactivity in the Geiger-Müller counter.

Uracil was isolated from the PNA of the regenerating liver according to methods worked out at this laboratory \(^5\). The uracil was probably contaminated with cytosine that had undergone deamination to uracil during the preparation.

After the degradation procedure described above the samples obtained were analyzed in the Geiger-Müller counter. The results are given in Table 1.

Table 1.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>counts/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>28 000</td>
</tr>
<tr>
<td>Mean value of respiratory CO₂</td>
<td>2 880</td>
</tr>
<tr>
<td>Uracil</td>
<td>35</td>
</tr>
<tr>
<td>Carbon atom 2</td>
<td>62</td>
</tr>
<tr>
<td>Carbon atoms 5 and 6</td>
<td>9</td>
</tr>
<tr>
<td>Carbon atom 4</td>
<td>60</td>
</tr>
</tbody>
</table>

These results indicate that in regenerating liver the carbon from bicarbonate enters positions 2 and 4 in the pyrimidine ring to the same degree. Wilson has previously found that bicarbonate enters position 2 (personal communication to professor Hammarsten) and his findings are confirmed by this investigation.

A more detailed report of the method and the experiment with C¹⁴-bicarbonate will be published later.

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The Absorption of Ultraviolet Light by Enterogastrone

A preliminary report

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It has been found that an enterogastrone preparation from intestines of hogs, which contains no amino acids or peptides (biuret and ninhydrin reactions negative) and has a nitrogen content of 0.24%, shows a characteristic absorption curve in the ultraviolet region. It has a maximum at 2600 Å and a minimum at 2350 Å. Evidence has been obtained, that this absorption curve is due to the active enterogastrone molecule. It was found that the decrease in biological activity which occurred when the extract was dissolved in water and stored at room temperature (probable due to bacterial activity) was accompanied by a decrease in the extinction at 2600 Å. A detailed description of the experiments and a full discussion of the results will shortly appear in this journal.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>H−X dist.</th>
<th>Dissociat. energy</th>
<th>C</th>
<th>Δ</th>
<th>r₂</th>
<th>Ionic radii*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r₁</td>
<td></td>
<td>dyne/cm</td>
<td></td>
<td></td>
<td>Pauling</td>
</tr>
<tr>
<td>HF</td>
<td>0.92 Å</td>
<td>6.1 e.v.</td>
<td>9.7 · 10⁵</td>
<td>0.45 Å</td>
<td>1.37 Å</td>
<td>1.36 Å</td>
</tr>
<tr>
<td>HCl</td>
<td>1.28 Å</td>
<td>4.43 e.v.</td>
<td>5.15 · 10⁵</td>
<td>0.52 Å</td>
<td>1.80 Å</td>
<td>1.81 Å</td>
</tr>
<tr>
<td>HBr</td>
<td>1.41 Å</td>
<td>3.60 e.v.</td>
<td>4.11 · 10⁵</td>
<td>0.53 Å</td>
<td>1.94 Å</td>
<td>1.95 Å</td>
</tr>
<tr>
<td>HJ</td>
<td>1.60 Å</td>
<td>2.75 e.v.</td>
<td>3.14 · 10⁵</td>
<td>0.53 Å</td>
<td>2.13 Å</td>
<td>2.16 Å</td>
</tr>
<tr>
<td>HH</td>
<td>0.74 Å</td>
<td>4.48 e.v.</td>
<td>5.9 · 10⁵</td>
<td>0.50 Å</td>
<td>1.24 Å</td>
<td>2.08 Å</td>
</tr>
</tbody>
</table>

We may perhaps understand this by considering the distance r₂ as the boundary for interference between electrons belonging to the halogen and those belonging to another electronic system. As the proton approaches r₂ from r₁ the electron cloud is polarized and finally — at r₂ — it is just about being deprived of one electron. But if an electron belonging to a “stable” cation tries to get inside the limiting sphere of the halide ion the resulting electronic interaction will give an antibonding effect so that usually the ionic crystal will be more stable than the molecular state. (As the proton has no electrons there will be no antibonding effect when it enters the position inside the limiting sphere giving minimum of electrostatic energy.) This point of view is in essential agreement with our ideas about ionic crystals according to which the interionic distances are determined by the condition that the energy shall be a minimum and the electron clouds of the ions must not inter-penetrate. But as it is only a very rough picture to reckon with a definite limit r₂ for electronic interaction in the hydrogen halides it may, perhaps, be concluded that the ionic radii to the same extent represent idealized concepts.


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