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# DISSOCIATION ENERGIES OF AXIAL AND EQUATORIAL CARBON-CARBON BONDS IN SUBSTITUTED DECAHYDROQUINOLOLS

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Spectral data (i.r., n.m.r., mass spectrometry) of various cyclic compounds indicate that dissociation energies of axial and equatorial bonds should differ. In the present communication we report on the application of appearance potentials (AP) for quantitative evaluation of dissociation energy differences between axial and equatorial carbon-carbon bonds in substituted decahydroquinol-4-ols.

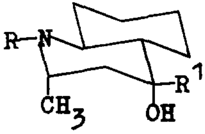
From mass spectrometric data, the bond dissociation energy can be calculated by the equation:

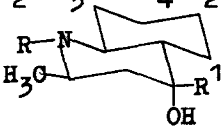
$$D[R_1-R_2] = AP[R_1^{+}] - IP[R_1^{\bullet}] - E^{*}[R_1^{+}, R_2^{\bullet}] - E^{*}_{kin}[R_1^{+}, R_2^{\bullet}]$$

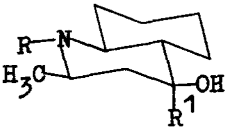
where $AP[R_1^{+}]$ is the appearance potential of the $[R_1^{+}]$ ion, $IP[R_1^{\bullet}]$ is the ionization potential of the $[R_1^{\bullet}]$ radical, $E^{*}$ and $E^{*}_{kin}$ are the vibrational and kinetic energies of the $[R_1^{+}]$ and $[R_2^{\bullet}]$ fragments.

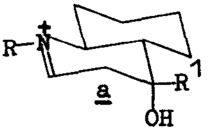
If the electron-impact induced fragmentation of two epimeric molecules (A) and (B) with differing orientation of a given carbon-carbon bond proceeds through cleavage of this bond, the formation of common $[R_1^{+}]$ ions and $[R_2^{\bullet}]$ radicals occurs. In such case, the $IP[R_1^{\bullet}]$ values should be equal for the epimers. The $E^{*}$ and $E^{*}_{kin}$ values are most likely to be also equal for the epimers (A) and (B). Hence the equality $D[R_1-R_2]_A - D[R_1-R_2]_B = AP[R_1^{+}]_A - AP[R_1^{+}]_B$ should determine the difference between the dissociation energies of axial and equatorial bonds.

Earlier[1,2] we had determined mass spectrometrically the stereochemistry of 1,2-dimethyl- and 1-ethyl-2-methyl-4-alkyldecahydroquinol-4-ols (1-3). Relative intensities of the $[M-CH_3]^{+}$ (a) and $[M-C_2H_5]^{+}$ (b) ions the formation of which is associated with the loss of only 2-$CH_3$ and 4-$C_2H_5$ groups, respectively, had led to conclusion that axial 2-$CH_3$ and 4-$C_2H_5$ are eliminated more readily than equatorial from the molecular ions of these epimers. This could mean that the dissociation energies of the axial $C_2$-$CH_3$ and $C_4$-$C_2H_5$ bonds are lower than these of the equatorial bonds. Since for the pairs of epimers the ions a and b are each identical the ionization potentials of the corresponding radicals are equal as are the values $E^*$ and $E^*_{kin}$ of the fragments resulting from the decomposition. Thus, the difference between the AP's of the a or b ions for the epimers should be equal to the difference between the dissociation energies of the axial and equatorial $C_2$-$CH_3$ or $C_4$-$C_2H_5$ bonds, respectively.

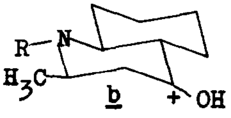








| | | | | |
|---|---|---|---|---|
| 1a | $R{=}CH_3$, $R^1{=}C{\equiv}CH$ | 2a | | |
| 1b | $R{=}CH_3$, $R^1{=}CH{=}CH_2$ | 2b | | |
| 1c | $R{=}CH_3$, $R^1{=}C_2H_5$ | 2c | $R{=}CH_3$, $R^1{=}C_2H_5$ | 3c |
| | | 2d | $R{=}R^1{=}C_2H_5$ | 3d |



Using the electron impact method [3] we measured the AP's of the a and b ions with rather good reproducibility [4]. The Table shows that the dissociation energies of the axial $C_2$-$CH_3$ bonds are almost 3 Kcal/mole lower than those of the equatorial bonds.

TABLE

| Compound | $AP/M-CH_3/^+$ ev | $\Delta D(C_2-CH_3)$ Kcal/mole | $AP/M-C_2H_5/^+$ ev | $\Delta D(C_4-C_2H_5)$ Kcal/mole |
|---|---|---|---|---|
| 1a | 9,15 | 4,15±1,15 | - | |
| 2a | 9,33 | | - | |
| 1b | 8,98 | 3,69±0,92 | - | |
| 2b | 9,14 | | - | |
| 1c | 9,00 | 3,46±0,92 | - | |
| 2c | 9,15 | | 9,94 | 0,46±0,69 |
| 3c | - | | 9,92 | |
| 2d | - | | 9,90 | 1,15±0,92 |
| 3d | - | | 9,85 | |

In the case of axial and equatorial $C_4$-$C_2H_5$ bonds the dissociation energies are essentially the same within the experimental error (Table). Thus, the suggestion can be made that the observed dissociation energy difference is peculiar to only the axial and equatorial bonds linked to α-C atom relatively to nitrogen.

## REFERENCES AND FOOTNOTES

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4. Mean error is about ±0,02 ev. The measurements were made on a LKB-2091 mass spectrometer by the simultaneous introduction of the sample through the direct inlet (30°) and of the reference (benzene, IP=9,25 ev) through the heated inlet (200°). The temperature of the ionization chamber was 200°. The AP's observed may differ from the absolute values but, in our opinion, they reflect the true difference between the AP's.