Molecular Formula and Degree of Unsaturation

A RELATION stated without proof or reference by Soffer[1] deserves to be better known. Ideas more or less equivalent to it seem to be widely known to organic chemists, but workers in related fields may find the result useful when dealing with organic compounds. This communication presents a proof, together with some remarks on interpretation and use (supplementary to Soffer's remarks).

For a start, consider a molecule the molecular (numerical) formula of which is known, and the atoms of which can safely be regarded as covalent with predictable valencies. Thus we can calculate the sum V of the valencies of all the atoms. The number of bonds in the structure must be $\frac{1}{2} V$ because each bond satisfies two valencies.

But if there are N atoms then as few as $N - 1$ bonds are sufficient to link them together—one bond would serve to link two atoms, a second bond would allow a third atom to be added, and so on.

If this were fewer than $\frac{1}{2} V$, then each of the extra bonds must link atoms which are already linked either directly or indirectly in the molecule. If indirectly, then such an extra bond completes a ring; if directly, it gives us a double bond (or increases the order of a multiple bond). Always we get what Soffer calls a "cyclic element of structure". (A triple bond is to be counted as two cyclic elements.) Thus the number of these cyclic elements is predicted as the number of 'surplus' bonds:

$$\rho \; (\text{say}) \; = \; \tfrac{1}{2} V - N + 1 \tag{1}$$

Also 2ρ is the number of added hydrogens required to saturate the molecule (eliminating all bond-duplications and rings): because each pair of hydrogens eliminates one of the 'surplus' bonds.

(1) We see that two molecules have the same ρ-value whenever their molecular formulæ are identical (isomeric): or when the formulæ differ only by multiples of CH_2, NH and/or O, because these combinations contribute zero to $(\frac{1}{2} V - N)$.

(2) Equation (1) may be written:

$$\rho = \tfrac{1}{2} \Sigma v n_v - \Sigma n_v + 1$$

where n_v is the number of atoms of valency v, and rearranged to give Soffer's form:

$$\rho = 1 + \tfrac{1}{2} \Sigma n_v (v - 2) \tag{2}$$

(that is, $\rho = 1 + \frac{1}{2} (2n_4 + n_3 - n_1)$ if no higher valencies are present). This gives a quicker calculation if it can be remembered.

(3) Soffer's definition, "in counting the number of cyclic structures in a polycyclic system no cyclic structure is counted if it is made up entirely of elements of other cyclic structures which themselves have been counted", can give ambiguous results in some cases. Thus tetradecahydroanthracene, $C_{14}H_{24}$, gives $\rho = 3$ and has indeed three six-membered rings:

but could be counted as having only two rings, the middle one and the 'outside'. In such a case, we must say that ρ predicts the number of bonds that must be cut to eliminate all the cyclic structures. (For formally planar structures it is sufficient to count non-overlapping rings.)

(4) The equation holds if the true structure has the atoms in their predicted covalencies, or if an acceptable model of the structure has this property. Thus aromatic nuclei may be considered as having Kekulé structures, as Soffer apparently intends when he cites benzylpenicillin and strychnine. (Alternatively we may arbitrarily call each aromatic (π) electron-pair a 'cyclic structure'.) A benzene ring is a possible explanation of four units of a calculated unsaturation.

Similar considerations apply to the groups —NO and —NO₂ (count one cycle each); but substituted ammonium is more difficult to deal with as it appears 'supersaturated' until we calculate again using valency five for the nitrogen.

(5) The equation may be generalized to a set of atoms other than a single complete molecule. By adding equations for M separate molecules we obtain:

$$\rho = \tfrac{1}{2} V - N + M \quad \text{or} \quad \rho - M = \tfrac{1}{2} V - N$$

where N, V, ρ are the total number of atoms, valencies and cyclic elements in the M molecules. Here M replaces the 1 of equation (1) (or (2), similarly). On the other hand, we must subtract $\frac{1}{2}$ from the same figure for each valency either not satisfied (as in a free radical), or not satisfied within the set of atoms (such as the monomeric unit of a dimer or polymer, or 'structural units' of coal[2]).

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[1] Soffer, M. D., Science, 127, 880 (1958).
[2] van Krevelen, D. W., Coal, 436 (Amsterdam, Elsevier, 1961).

Near Ultra-violet Absorption Spectra of o-, m-, and p-Fluorophenol Vapour

THE absorption spectra of o-, m-, and p-fluorophenol in vapour phase have been examined with a Hilger E_1 large quartz spectrograph. A number of plates were taken with different cell lengths and at temperatures ranging from 26° C to 60° C; while the temperature of the reservoir containing the substance varied from − 15° C to 60° C. The bands in each case appear well defined with the cell of length 70 cm maintained at temperature 26° C. A hydrogen lamp was used as the source of continuum for the ultra-violet region. Ilford special rapid N.40 plates were used to photograph the spectra in about half an hour.

Nearly 300 bands have been photographed in each case. The intense bands are double headed, similar to those observed in the case of phenol. The mean doublet separation in all the three spectra is found to be of the order of 10 cm⁻¹.

o-Fluorophenol: This molecule belongs to symmetry class Cs to a first approximation and its absorption spectrum is due to the electronic transition $^1A' \leftarrow {}^1A'$. The most intense band at 36,802 cm⁻¹ has been chosen as the (0, 0) band, and the entire spectrum analysed in terms of the frequencies 239, 415, 566 and 766 cm⁻¹ in the ground state and 291, 506, 718, 945, 1,040 and 1,128 cm⁻¹ in the excited state. The ground state frequencies correspond fairly closely to the known Raman frequencies.

m-Fluorophenol: The meta-derivative of the molecule can also be taken to belong to the symmetry class C_s and the bands may be attributed to the electronic transition $^1A' \leftarrow {}^1A'$ which is an allowed transition. The intense band at 36,620 cm⁻¹, which is observed with still greater intensity at low temperature, is taken to be the (0, 0) band. The entire spectrum is analysed in terms of two ground state frequencies, 427 and 741 cm⁻¹, and six excited state frequencies, 146, 206, 254, 713, 976 and 1,175 cm⁻¹.

p-Fluorophenol: The para-derivative belongs to C_{2v} symmetry class approximately, and the observed spectrum involves the electronic transition $^1A_1 \leftarrow {}^1B_1$, which is allowed with the transition moment lying in the molecular plane and perpendicular to C—OH bond. The most intense band at 35,132 cm⁻¹, which appears with increased intensity at lower temperatures, has been taken to be the (0, 0) band. The bands have been analysed in terms of three ground state frequencies 251, 466 and 865 cm⁻¹, and seven excited state frequencies, 356, 413, 569, 838, 875, 1,205 and 1,273 cm⁻¹. Satisfactory correspondence of the