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Mass Spectral Interpretation Using the "Rule of '13' "

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A simple method for the determination of potential chemical formulae for a given molecular weight has been developed in undergraduate and graduate spectroscopic identification courses at the University of Houston at Clear Lake City. This procedure has proven to be a useful supplement to the conventional methods of mass spectral interpretation.

Description of the Procedure

The procedure is based on the application of chemical logic and is called "The Rule of '13.' " The first step in "The Rule of '13' " is to consider only carbon and hydrogen as being present in the molecule so the number "13" represents the sum of the atomic weights of one carbon atom and one hydrogen atom. The theoretical number of carbons and hydrogens present is found by dividing the molecular weight (M), which can be obtained by locating the molecular ion in the mass spectrum, by 13 resulting in a numerator(n) and a remainder(r).

$$M/13 = n + r/13$$

A base formula for the given molecular weight which consists of only carbon and hydrogen is then obtained by application of the formula

$$C_n H_{n+r}$$

The degree of unsaturation(u), representing the number of double bonds and/or rings present in the potential molecule, is obtained from the formula

$$u = (n - r + 2)/2$$

Application of the Procedure

A simple application of "The Rule of '13' " could result from the observation of a molecular ion at mass 78 in a mass spectrum.

$$\begin{array}{rrl} & 6 & n \\ 13 \,\big)\!\!\! & \overline{78} & m \\ & -78 & \\ & 0 & r \end{array}$$

The base formula is then $C_6 + H_{6+0}$ or C_6H_6 from the formula $C_n H_{n+r}$. The degree of unsaturation from $u = (n - r + 2)/2$ is $(6 - 0 + 2)/2 = 4$. The formula C_6H_6 with four degrees of unsaturation would represent benzene provided that other information present in the mass spectrum supported this conclusion.

Substitution of Carbon-Hydrogen Equivalents

Chemical formulas containing elements other than carbon and hydrogen can be obtained by subtracting the carbon/hydrogen mass equivalent of the element of interest from the base formula before adding the selected element. For example, CH_4(mass 16) could be replaced by oxygen(O) while CH_2(mass 14) could be replaced by nitrogen(N). The table contains the data necessary to make these substitutions, including appropriate Δu values for adjusting the degrees of unsaturation, for some of the more common elements in organic compounds.

Data for Substituting Some Common Elements in Organic Compounds in Rule of 13 Calculations

Element	C/H Equivalent	Δu	$-\Delta\%(M+1)$	$-\Delta(\Delta m) \times 10^3$
C	H_{12}	7	−1.1	93.90
H_{12}	C	−7	1.1	−93.90
O	CH_4	1	1.1	36.38
N	CH_2	½	0.7	12.58
N_2	C_2H_4	1	1.4	25.15
S(+2)	C_2H_8	2	1.4	90.25
Cl	C_2H_{11}	3	2.2	117.22
^{79}Br	C_6H_7	−3	6.6	136.45
^{79}Br	C_5H_{19}	4	5.5	230.35
F	CH_7	2	1.1	56.37
Si	C_2H_4	1	−2.9	54.37
P	C_2H_7	2	2.2	81.01
I	C_9H_{19}	0	9.9	244.20
I	$C_{10}H_7$	7	11.0	150.30

The values presented in the table for Δu were obtained from

$$\Delta u = \frac{j(B-2) - 2C + H}{2}$$

where j is the number of atoms being added ($j = 2$ for N_2, 12 for H_{12} and 1 for the other elements presented in the table). B is the number of bonds formed by the added atom while C and H are the number of carbons and hydrogens substracted. The normal formula for u can also be used to calculate the values directly.

$$u = \frac{2C + 2 - H + j\Sigma(B-2)}{2}$$

The sum is taken over all elements except carbon and hydrogen.

An example of the substitution process can be demonstrated by selecting mass 142. Applying the formulae presented previously to mass 142 results in a base formula of $C_{10}H_{22}$ with zero degrees of unsaturation. Substitution of other elements for carbon/hydrogen using information from the table results in the following:

$$\begin{array}{lc} & u \\ C_{10}H_{22} & 0 \\ \underline{-C_1H_4 + O} & \underline{+1\ (\Delta u)} \\ C_9H_{18}O & +1 \\ C_{10}H_{22} & 0 \\ \underline{-C_2H_{11} + Cl} & \underline{+3\ (\Delta u)} \\ C_8H_{11}Cl & +3 \\ C_{10}H_{22} & 0 \\ \underline{-C_2H_4 + N_2} & \underline{+1\ (\Delta u)} \\ C_8H_{18}N_2 & +1 \end{array}$$

[1] Work done in partial fulfillment of the requirements for the Master's of Science Degree.

The requirement for substitution of other elements for carbon and hydrogen could result from inspection of the mass spectrum, combustion analysis, available IR or NMR data, etc.

"The Rule of '13' " can also direct the analyst to make certain substitutions. The nitrogen rule, which simply states that a single or other odd number of nitrogens in a molecule requires that the molecule have an odd mass, is automatically incorporated in "The Rule of '13' ", since an odd molecular weight always results in a fractional value for u. Therefore, a fractional value for u automatically indicates the presence of a single or other odd number of nitrogens in the molecule. The presence of oxygen and/or nitrogen is often indicated by the calculation of a negative value of u.

Calculations for mass 74 result in a base formula of C_5H_{14} with minus one degrees of unsaturation. This negative value for u indicates that at least one oxygen or two nitrogens are present.

$$
\begin{array}{ll}
 & u \\
C_5H_{14} & -1 \\
\underline{-C_2H_8 + O_2} & \underline{+2\ (\Delta u)} \\
C_3H_6O_2 & +1
\end{array}
\quad \text{or} \quad
\begin{array}{ll}
 & u \\
C_5H_{14} & -1 \\
\underline{-C_2H_4 + N_2} & \underline{+1\ (\Delta u)} \\
C_3H_{10}N_2 & 0
\end{array}
$$

Exactly which one of the above possibilities is correct could be determined by close inspection of the mass spectrum or from inspection of IR or NMR data since the analyst has been directed by "The Rule of '13' " to look for certain functional groups. If available IR data indicates the presence of a carbonyl (characterized by distinctive absorption in the 1580–1900 cm^{-1} region) then the u value must be at least one, and the presence of two oxygens or one oxygen and two nitrogens is indicated.

$$
\begin{array}{ll}
 & u \\
C_5H_{14} & -1 \\
\underline{-C_2H_8 + O_2} & \underline{+2\ (\Delta u)} \\
C_3H_6O_2 & +1
\end{array}
\quad \text{or} \quad
\begin{array}{ll}
 & u \\
C_5H_{14} & -1 \\
\underline{-CH_4 + O} & \underline{+1\ (\Delta u)} \\
C_4H_{10}O & 0 \\
\underline{-C_2H_4 + N_2} & \underline{+1\ (\Delta u)} \\
C_2H_6ON_2 & +1
\end{array}
$$

The presence and number of bromine and chlorine atoms can generally be obtained from the isotopic distribution (M + 2, M + 4, etc.) which is given in most textbooks. Also, the isotopic distribution for chlorine and bromine can be obtained from the binomial theorem using Pascal's Triangle, which is normally introduced in the discussion of proton magnetic resonance.

$$
\begin{array}{c|ccccccccc}
n & & & & & 1 & & & & \\
0 & & & & 1 & & 1 & & & \\
1 & & & 1 & & 2 & & 1 & & \\
2 & & 1 & & 3 & & 3 & & 1 & \\
3 & 1 & & 4 & & 6 & & 4 & & 1 \\
4 & & & & & & & & &
\end{array}
$$

Pascal's Triangle

The relative intensities of the 79 and 81 isotopes of bromine are nearly equal so the distribution can be taken from the triangle. For example, for four bromines, the distribution is 1:4:6:4:1. For chlorine, the distribution of the 35 isotope to the 37 isotope is approximately 3:1, so the coefficients must be multiplied by 3^n, 3^{n-1}, etc. As an example, for $n = 4$, the distribution is $1 \times 81{:}4 \times 27{:}6 \times 9{:}4 \times 3{:}1 \times 1$ or 81:108:54:12:1.

If there are mixtures of chlorine and bromine then the easiest procedure is to obtain the distribution for each of the elements and simply to multiply the two. For example, for a compound with Cl_2Br_3, the bromine distribution is 1:3:3:1, while that for chlorine is 9:6:1. The product is then

$$
\begin{array}{cccccc}
 & & 1 & 3 & 3 & 1 \\
 & & & 9 & 6 & 1 \\
\hline
 & & 1 & 3 & 3 & 1 \\
 & 6 & 18 & 18 & 6 & \\
9 & 27 & 27 & 9 & & \\
\hline
9 & 33 & 46 & 30 & 9 & 1
\end{array}
$$

If one chlorine and one bromine are indicated and the molecular weight is 190, then the base formula is $C_{14}H_{22}$ with $u = 4$.

$$
\begin{array}{ll}
 & u \\
C_{14}H_{22} & 4 \\
\underline{-C_2H_{11} + Cl} & \underline{+3\ (\Delta u)} \\
C_{12}H_{11}Cl & +7 \\
\underline{-C_6H_7 + Br} & \underline{-3\ (\Delta u)} \\
C_6H_4ClBr & +4
\end{array}
$$

In the undergraduate course, only C, H, ON, S, Cl, and Br are considered. In the graduate course F, Si, P, and I are added to the list. Also, the incremental values for the %(M + 1) and the exact masses can be calculated for the carbon/hydrogen equivalents and are included in the table. The values for the base quantities are given by

$$m_{\text{exact,base}} = m + 7.825 \times 10^{-3}(n + r)$$

$$m_{\text{exact}} = m_{\text{exact,base}} + \Delta(\Delta m)$$

$$\%(M + 1)_{\text{base}} \cong 1.1(n)$$

$$\%(M + 1) = \%(M + 1)_{\text{base}} + \Delta\%(M + 1)$$

The increments for these quantities have been calculated and are shown in the table outside the double lines. If the $M + 1$ data are of high quality, then the number of carbon atoms can be determined, or, if the exact mass is given, then the presence of certain atoms can be deduced.

Consider a compound with exact mass 162.116; the base data is

Formula	u	$\%(M + 1)$	$\Delta m \times 10^{+3}$
$C_{12}H_{18}$	4	13.2	140
$-C_2H_4 + N_2$	$+1\ (\Delta u)$	$-1.4\ (\Delta)$	$-25.15\ \Delta(\Delta m)$
$C_{10}H_{14}N_2$	+5	11.8	114.85

The use of the $\Delta\ \%(M + 1)$ is obvious and is not illustrated. If desired, $\%(M + 1)$ and $\%(M + 2)$ can be calculated from the standard formulae

$$\%(M + 1) \cong 1.1(\#C) + 0.36(\#N) + 0.78(\#S) + 5.10(\#Si)$$

$$\%(M + 2) \cong 0.006(\#C)^2 + 0.20(\#O) + 4.40(\#S) + 3.35(\#Si)$$

These formulas are useful in distinguishing between S and Si once it is noted that the $\%(M + 2)$ is abnormally high.

Summary

Using "The Rule of '13' " and the table it is possible to obtain all of the potential formulas for a given molecular weight and to calculate all of the typical mass spectrometric parameters which are obtained experimentally. The calculated values can then be compared to the experimental values to obtain the most reasonable formula. Often it is necessary to have access to IR, UV, and NMR data to make this determination.