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New Approach for Assigning Mean Oxidation Number of Carbons to Organonitrogen and Organosulfur Compounds

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Research article

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New approach for assigning mean oxidation number of carbons to organonitrogen and organosulfur compounds

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Abstract: Organonitrogen and organosulfur compounds are abundant in the natural environment. To understand the biological redox pathways properly, it is important for learners to be able to count the oxidation number of organic carbons. However, the process of counting is not always easy. In addition, organonitrogen and organosulfur molecules are seldom studied. To compensate these problems, this paper explores the bond-dividing method, which can effectively determine the mean oxidation number of carbons of organonitrogen and organosulfur molecules. This method uses the cleavage of carbon-sulfur and carbon-nitrogen bonds to obtain the organic and inorganic fragments. The mean oxidation numbers of carbon atoms, nitrogen atoms, and sulfur atoms can be calculated by the molecular formulas of their fragments. Furthermore, when comparing organosulfur or organonitrogen molecules in a redox conversion, the changes of the mean oxidation numbers of carbon atoms, nitrogen atoms, and sulfur atoms can be used as indicators to identify the redox positions and determine the number of transferred electrons.

Keywords: mean oxidation number of carbons; molecular formula; organonitrogen compound; organosulfur compound; structural formula.

Introduction

Redox reaction is a fundamental area in the study of chemistry and biochemistry (Goodstein, 1970; Ochs, 2019). Organonitrogen compounds (ONC) and organosulfur compounds (OSC) are abundant in the natural environment. Many of them participate in the biochemical redox pathways (Francioso, Conrado, Mosca & Fontana, 2020; Shapir et al., 2007). To understand any bio-redox process, the quantity of transferred electrons has to be studied. The concept used for counting transferred electrons is oxidation number (or the oxidation state), which is applied for defining and balancing redox reactions.

Oxidation number (ON) is defined as “the atom’s charge after ionic approximation of its heteronuclear bonds” (Karen, McArdle & Takats, 2014, 2016). Lewis formula method (Kauffman, 1986; Loock, 2011; Minkiewicz, Darewicz & Iwaniak, 2018), structural formula method (Bentley, Franzen & Chasteen, 2002; Halkides, 2000; Jurowski, Krzeczkowska & Jurowska, 2015; Menzek, 2002), and molecular formula method (Eggert, Middlecamp & Kean, 2014; Holleran & Jespersen, 1980; Jurowski et al., 2015; Menzek, 2002) have all been used to count the oxidation numbers of atoms. Lewis formula and structural formula methods can be applied to determine individual oxidation number of atoms; and the molecular formula method is widely used in textbooks for assigning the mean oxidation number of atoms (Chang & Goldsby, 2013; Tro, 2014). However, the

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mean oxidation number of carbons (ONc) of ONC and OSC are seldom studied (Menzek, 2002; Jurowski et al., 2015).

The basic rule of the molecular method is that the sum of all oxidation number of atoms in a molecule or an ion is equal to its charge. The mathematical relationship is charge = ΣON_i.

For molecules:	charge = 0; 0 = ΣON_i
For ions:	charge ≠ 0; charge = ΣON_i

Although the molecular formula method is straightforward, it is not applicable to all cases. For instance, ON of nitrogen and sulfur atoms can range from −3 to +5 and from −2 to +6 respectively. However, the rule assumes ON of nitrogen and sulfur atoms to be −3 and −2 respectively when counting the mean ON of organic carbons. This will cause error in calculation of the mean ON of organic carbons. To compensate these problems, this paper explores a new approach for determining the mean ON of organic carbons. Its operating procedures and examples are given.

Heterolytic bond cleavages and fragments

This new approach is called the bond-dividing method. It is based on the concept of the heterolytic bond cleavage and its divided fragments. In a heterolytic bond, there are two bonded atoms which exhibit different electronegativities. The cleavage of the atom group which is more electronegative becomes negative fragments whereas the cleavage of the atom group which is less electronegative becomes positive fragments.

For neutral ONC and OSC molecules, the cleavage of heterolytic C–N/C=N/C≡N ($\chi C < \chi N$) bonds and C–S/C=S/C≡S ($\chi C < \chi S$) bonds forms charged fragments. Their cationic organic fragment and anionic inorganic fragment can be obtained. Examples of charged organic fragments and inorganic fragments containing nitrogen atoms or sulfur atoms are given in Table 1.

Table 1: Examples of carbon-nitrogen and carbon-sulfur heterolytic bonds cleavages.

Neutral ONC	Fragments	Neutral OSC	Fragments
$R{-}NH_2$	$R^+ + {}^-NH_2$	R–S–R′	$R^+ + S^{-2} + {}^+R'$
R′CH=NH	$R'CH^{+2} + {}^{-2}NH$	$R_2C{=}S$	$R_2C^{2+} + {}^{-2}S$
$CH_3C{\equiv}N$	$CH_3C^{+3} + {}^{-3}N$	HC≡SOH	$HC^{+3} + {}^{-3}SOH$
$R_2N{=}NR'_2$	$R^+ + R^+ + {}^{-2}N{=}N^{-2} + R'^+ + R'^+$	R–S–S–R′	$R^+ + {}^-SS^- + {}^+R'$

By using charged organosulfur particles as examples, the cleavage of carbon and sulfur heterolytic bonds forms neutral or cationic organic fragments.

$$CH_3C(O)CH^-SO_2CH_3 \rightarrow CH_3C(O)CH + SO_2^{-2} + {}^+CH_3$$
$$CH_3CH_2S^+H_2 \rightarrow CH_3CH_2^+ + SH_2$$

Bond-dividing method for counting the mean ON

A structural formula is required to determine the mean ONc of ONC and OSC. Based on the known bond connectivity and bond order between carbon-nitrogen and carbon-sulfur in a structural formula, the carbon-nitrogen and carbon-sulfur bonds are divided to form organic fragments and inorganic fragments. Then the mean ONc, ONs, and ONn can be counted by their molecular formulas. When using the molecular formula for counting the mean ON, the values of ONh (hydrogen cation) and ONo (oxide) are +1 and −2 respectively. Atomic electronegativities by Pauling scale are placed in the order of $\chi H < \chi C < \chi S < \chi N < \chi O$. The mean ON can be named and calculated by using the mathematical equation of charge = ΣON_i, even if the number of carbon atoms (n_C), sulfur atoms (n_S), or nitrogen atoms (n_N) is equal to one. After dividing the bonds, a molecular formula of the organic fragment is resulted by summating all individual organic fragment's molecular formula. The operating procedures are as follows:

a. Divide all carbon-nitrogen and carbon-sulfur bonds into fragments
b. Calculate the mean ON_C of the organic fragment
c. Calculate the mean ON_S and/or ON_N of the inorganic fragment(s)

Example 1 Given condensed structural formula, $CH_3CH_2SSCH_2CH_3$

Step 1. cleavage of C–S bonds: $CH_3CH_2SSCH_2CH_3$

$CH_3CH_2SSCH_2CH_3 \rightarrow CH_3CH_2^+ + {}^-SS^- + {}^+CH_2CH_3$

Step 2. organic fragments: $CH_3CH_2^+ + {}^+CH_2CH_3$

$CH_3CH_2^+ + {}^+CH_2CH_3 = C_4H_{10}^{+2}$

charge = $n_C ON_C + n_H ON_H$

$$\text{mean } ON_C \text{ of } C_4H_{10}^{+2} = \frac{\text{charge} - n_H ON_H}{n_C} = \frac{(+2) - 10(+1)}{4} = -2$$

Step 3. inorganic fragment: S_2^{-2}

charge = $n_S ON_S$

$n_S = 2$; charge = -2

$$\text{mean } ON_S \text{ of } S_2^{-2} = \frac{\text{charge}}{n_S} = \frac{(-2)}{2} = -1$$

Molecule	Organic fragment	Inorganic fragment
$CH_3CH_2SSCH_2CH_3$	$C_4H_{10}^{+2}$	S_2^{-2}
$C_4H_{10}S_2$		
mean ON	−2	−1

Example 2 Given condensed structural formula, $CH_3CH_2SCH_2CH_2SH$

Step 1. cleavage of C–S bonds: $CH_3CH_2SCH_2CH_2SH$

$CH_3CH_2SCH_2CH_2SH \rightarrow CH_3CH_2^+ + S^{-2} + {}^+CH_2CH_2^+ + {}^-SH$

Step 2. organic fragments: $CH_3CH_2^+ + {}^+CH_2CH_2^+$

$CH_3CH_2^+ + {}^+CH_2CH_2^+ = C_4H_9^{+3}$

charge = $n_C ON_C + n_H ON_H$

$$\text{mean } ON_C \text{ of } C_4H_9^{+3} = \frac{\text{charge} - n_H ON_H}{n_C} = \frac{(+3) - 9(+1)}{4} = -\frac{3}{2}$$

Step 3. inorganic fragments: S^{-2} and SH^{-}

For S^{-2}

charge = $n_S ON_S$

$n_S = 1$; charge = −2

$$\text{mean } ON_S \text{ of } S^{-2} = \frac{\text{charge}}{n_S} = \frac{(-2)}{1} = -2$$

For SH^{-}

charge = $n_S ON_S + n_H ON_H$

$n_S = 1$; $n_H = 1$; charge = −1

$$\text{mean } ON_S \text{ of } SH^{-} = \frac{\text{charge} - n_H ON_H}{n_S} = \frac{(-1) - 1(+1)}{1} = -2$$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment
$CH_3CH_2SCH_2CH_2SH$ $C_4H_{10}S_2$	$C_4H_9{}^{+3}$	S^{-2}	SH^{-}
mean ON	$-\frac{3}{2}$	−2	−2

Given the molecular formula of $C_4H_{10}S_2$, two of its selected isomers with different structural formulas of $CH_3CH_2SSCH_2CH_3$ (in Example 1) and $CH_3CH_2SCH_2CH_2SH$ (in Example 2) are provided.

The molecular formula of $CH_3CH_2SSCH_2CH_3$ (in Example 1) is $C_4H_{10}S_2$. The calculation of mean ON_C of $CH_3CH_2SSCH_2CH_3$ is shown.

$$4ON_C + 10ON_H + 2ON_S = 0$$

$$4ON_C + 10(+1) + 2(-1) = 0$$

$$ON_C = \frac{-8}{4} = -2$$

The molecular formula of $CH_3CH_2SCH_2CH_2SH$ (in Example 2) is $C_4H_{10}S_2$. The calculation of mean ON_C of $CH_3CH_2SCH_2CH_2SH$ is shown.

$$4ON_C + 10ON_H + 2ON_S = 0$$

$$4ON_C + 10(+1) + 2(-2) = 0$$

$$ON_C = \frac{-6}{4} = -\frac{3}{2}$$

When the mean ON_S of example 1 and example 2 are different, their mean ON_C will also be different even though they have the same molecular formula.

Example 3 Given condensed structural formula, $CH_3CH_2NO_2$

Step 1. cleavage of C–N bond: $CH_3CH_2NO_2$

$CH_3CH_2NO_2 \rightarrow CH_3CH_2^{+} + {}^{-}NO_2$

Step 2. organic fragment: $CH_3CH_2^+$

$CH_3CH_2^+ = C_2H_5^+$

charge = $n_C ON_C + n_H ON_H$

$$\text{mean } ON_C \text{ of } C_2H_5^+ = \frac{\text{charge} - n_H ON_H}{n_C} = \frac{(+1) - 5(+1)}{2} = -2$$

Step 3. inorganic fragment: NO_2^-

charge = $n_N ON_N + n_O ON_O$

$n_N = 1$; $n_O = 2$; charge = −1

$$\text{mean } ON_N \text{ of } NO_2^- = \frac{\text{charge} - n_O ON_O}{n_N} = \frac{(-1) - 2(-2)}{1} = +3$$

Molecule	Organic fragment	Inorganic fragment
$CH_3CH_2NO_2$	$C_2H_5^+$	NO_2^-
$C_2H_5O_2N$		
mean ON	−2	+3

Example 4 Given condensed structural formula, H_2NCH_2COOH

Step 1. cleavage of C–N bond: H_2NCH_2COOH

$H_2NCH_2COOH \rightarrow H_2N^- + {}^+CH_2COOH$

Step 2. organic fragment: ${}^+CH_2COOH$

${}^+CH_2COOH = C_2H_3O_2^+$

charge = $n_C ON_C + n_H ON_H + n_O ON_O$

$$\text{mean } ON_C \text{ of } C_2H_3O_2^+ = \frac{\text{charge} - n_H ON_H - n_O ON_O}{n_C} = \frac{(+1) - 3(+1) - 2(-2)}{2} = +1$$

Step 3. inorganic fragment: NH_2^-

charge = $n_N ON_N + n_H ON_H$

$n_N = 1$; $n_H = 2$; charge = −1

$$\text{mean } ON_N \text{ of } NH_2^- = \frac{\text{charge} - n_H ON_H}{n_N} = \frac{(-1) - 2(+1)}{1} = -3$$

Molecule	Organic fragment	Inorganic fragment
H_2NCH_2COOH	$C_2H_3O_2^+$	NH_2^-
$C_2H_5O_2N$		
mean ON	+1	−3

Even though $CH_3CH_2NO_2$ (in Example 3) and H_2NCH_2COOH (in Example 4) have the same molecular formula, $C_2H_5O_2N$, they have different mean ON_N and, therefore, different mean ON_C.

Counting the mean ON_C of $CH_3CH_2NO_2$ (in Example 3):

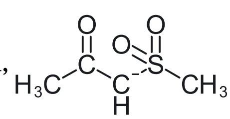
$$2ON_C + 5ON_H + 2ON_O + 1ON_N = 0$$
$$2ON_C + 5(+1) + 2(-2) + 1(+3) = 0$$
$$ON_C = \frac{-4}{2}$$
$$= -2$$

Counting the mean ON_C of H_2NCH_2COOH (in Example 4):

$$2ON_C + 5ON_H + 2ON_O + 1ON_N = 0$$
$$2ON_C + 5(+1) + 2(-2) + 1(-3) = 0$$
$$ON_C = \frac{2}{2}$$
$$= +1$$

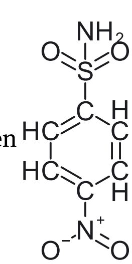
Simplified scheme for assigning the mean ON

In the simplified procedural scheme below, C stands for mean ON_C, H stands for mean ON_H, N stands for mean ON_N, and S stands for mean ON_S.

Example 5 Given molecular ion, 

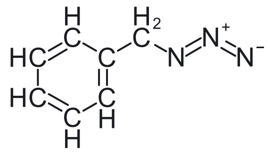
$$CH_3C(O)CH^-SO_2CH_3 \rightarrow CH_3C(O)CH + {}^-SO_2^- + {}^+CH_3$$
$$\rightarrow C_4H_7O^+ + SO_2^{-2}$$

Molecular ion	Organic fragment	Inorganic fragment
$CH_3C(O)CH^-SO_2CH_3$	$C_4H_7O^+$	SO_2^{-2}
$C_4H_7O_3S^-$		
mean ON	4C + 7H + 1O = +1	1S + 2O = −2
	4C + 7(+1) + 1(−2) = +1	1S + 2(−2) = −2
	C = −1	S = +2

Example 6 Given 

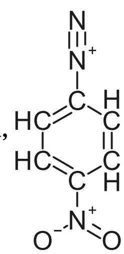
$$O_2NC_6H_4SO_2NH_2 \rightarrow O_2N^- + {}^+C_6H_4^+ + {}^-SO_2NH_2$$
$$\rightarrow NO_2^- + C_6H_4^{+2} + SO_2 + {}^-NH_2$$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment	Inorganic fragment
$O_2NC_6H_4SO_2NH_2$	$C_6H_4^{+2}$	NO_2^-	SO_2	NH_2^-
$C_6H_6O_4N_2S$				
mean ON	6C + 4H = +2	1N + 2O = −1	1S + 2O = 0	1N + 2H = −1
	6C + 4(+1) = +2	1N + 2(−2) = −1	1S + 2(−2) = 0	1N + 2(+1) = −1
	$C = -\frac{1}{3}$	N = +3	S = +4	N = −3

Example 7 Given 

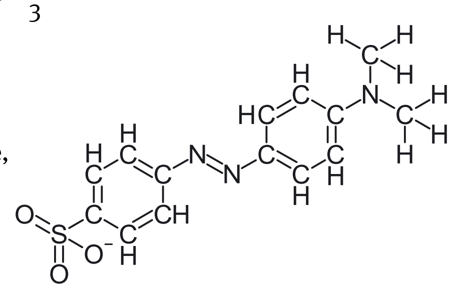
$$C_6H_5CH_2N_3 \rightarrow C_6H_5CH_2^+ + {}^-N_3$$
$$\rightarrow C_7H_7^+ + N_3^-$$

Molecule	Organic fragment	Inorganic fragment
$C_6H_5CH_2N_3$	$C_7H_7^+$	N_3^-
$C_7H_7N_3$		
mean ON	$7C + 7H = +1$	$3N = -1$
	$7C + 7(+1) = +1$	$N = -\frac{1}{3}$
	$C = -\frac{6}{7}$	

Example 8 Given diazonium, 

$$O_2NC_6H_4\ {}^+N{\equiv}N \rightarrow O_2N^- + {}^+C_6H_4^+ + N{\equiv}N$$
$$\rightarrow NO_2^- + C_6H_4^{2+} + N_2$$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment
$O_2NC_6H_4^+N{\equiv}N$	$C_6H_4^{2+}$	NO_2^-	N_2
$C_6H_4O_2N_3^+$			
mean ON	$6C + 4H = +2$	$1N + 2O = -1$	$2N = 0$
	$6C + 4(+1) = +2$	$1N + 2(-2) = -1$	$N = 0$
	$C = -\frac{1}{3}$	$N = +3$	

Example 9 Given methyl orange, 

$$\text{methyl orange} \rightarrow {}^-SO_3^- + {}^+C_6H_4^+ + {}^-N{=}N^- + {}^+C_6H_4^+ + {}^-N(CH_3)_2$$
$$\rightarrow SO_3^{-2} + C_6H_4^{2+} + N_2^{-2} + C_6H_4^{2+} + N^{-3} + CH_3^+ + CH_3^+$$
$$\rightarrow C_{14}H_{14}^{+6} + SO_3^{-2} + N_2^{-2} + N^{-3}$$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment	Inorganic fragment
methyl orange	$C_{14}H_{14}^{+6}$	SO_3^{-2}	N_2^{-2}	N^{-3}
$C_{14}H_{14}O_3N_3S^-$				
mean ON	$14C + 14H = +6$	$1S + 3O = -2$	$2N = -2$	$N = -3$
	$14C + 14(+1) = +6$	$1S + 3(-2) = -2$	$N = -1$	
	$C = -\frac{4}{7}$	$S = +4$		

Determining Δ mean ON in a redox conversion

The change of mean oxidation numbers of organic carbons (Δ mean ONc) has been established to define an organic redox reaction (Menzek, 2002). Regarding the redox conversions of ONC and OSC, changes of the mean ON of carbons, nitrogens, and sulfurs can be used as indicators for identifying the redox positions and counting the number of transferred electrons (Te^-) on the reacting atoms.

Δ mean ON = mean ON (product) – mean ON (reactant)

Δ mean ON > 0; oxidation

Δ mean ON = 0; non-redox reaction

Δ mean ON < 0; reduction

Te^- = n Δ mean ON

Te^- > 0; loss of electron; oxidation

Te^- = 0; non-redox reaction

Te^- < 0; gain of electron; reduction

For example, Δ mean ONc ≠ 0 represents there is a gain or loss of electrons on the carbon atoms and Δ mean ONn = 0 represents there is no gain or loss of electrons on the nitrogen atoms.

Example 10 Conversion: $C_6H_5NH_2 \rightarrow C_6H_5NO_2$

Reactant: $C_6H_5NH_2 \rightarrow C_6H_5^+ + {}^-NH_2$

Molecule	Organic fragment	Inorganic fragment
$C_6H_5NH_2$	$C_6H_5^+$	NH_2^-
mean ON	6C + 5H = +1	1N + 2H = –1
	6C + 5(+1) = +1	1N + 2 (+1) = –1
	$C = -\frac{2}{3}$	N = –3

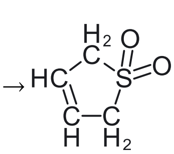
Product: $C_6H_5NO_2 \rightarrow C_6H_5^+ + {}^-NO_2$

Molecule	Organic fragment	Inorganic fragment
$C_6H_5NO_2$	$C_6H_5^+$	NO_2^-
mean ON	6C + 5H = +1	1N + 2O = –1
	6C + 5(+1) = +1	1N + 2 (–2) = –1
	$C = -\frac{2}{3}$	N = +3

Δ mean ONc = mean ONc ($C_6H_5^+$ from $C_6H_5NO_2$) – mean ONc ($C_6H_5^+$ from $C_6H_5NH_2$)
$= \left(-\frac{2}{3}\right) - \left(-\frac{2}{3}\right)$
= 0 (non-redox reaction on the carbon atoms)

Δ mean ONn = mean ONn (NO_2^-) - mean ONn (NH_2^-)
= (+3) – (–3)
= +6 (oxidation occurring on the nitrogen atom)

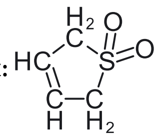
Te^- = nn Δ mean ONn
= (1) (+6)
= +6 (loss of 6 electrons on the nitrogen atom; oxidation)

Example 11 Conversion: $CH_2{=}CH{-}CH{=}CH_2 + SO_2 \rightarrow$ 

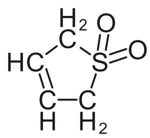
Reactants: $CH_2{=}CH{-}CH{=}CH_2$ and SO_2

Molecule $CH_2{=}CH{-}CH{=}CH_2$ SO_2
C_4H_6

mean ON	$4C + 6H = 0$	$1S + 2O = 0$
	$4C + 6(+1) = 0$	$S + 2(-2) = 0$
	$C = -\frac{3}{2}$	$S = +4$

Product:  $\rightarrow {}^{+}CH_2-CH{=}CH-CH_2^{+} + {}^{-}SO_2^{-}$

$\rightarrow C_4H_6^{+2} + SO_2^{-2}$

Molecule	Organic fragment	Inorganic fragment
 $C_4H_6O_2S$	$C_4H_6^{+2}$	SO_2^{-2}
mean ON	$4C + 6H = +2$	$1S + 2O = -2$
	$4C + 6(+1) = +2$	$1S + 2(-2) = -2$
	$C = -1$	$S = +2$

Δ mean ON$_C$ = mean ON$_C$ $(C_4H_6^{+2})$ – mean ON$_C$ (C_4H_6)

$= (-1) - \left(-\frac{3}{2}\right)$

$= +\frac{1}{2}$ (oxidation occurring on the carbon atoms)

Δ mean ON$_S$ = mean ON$_S$ (SO_2^{-2}) – mean ON$_S$ (SO_2)

$= (+2) - (+4)$

$= -2$ (reduction occurring on the sulfur atom)

Te^{-} = n_C Δ mean ON$_C$

$= (4)\left(+\frac{1}{2}\right)$

$= +2$ (loss of 2 electrons on the carbon atoms; oxidation)

Te^{-} = n_S Δ mean ON$_S$

$= (1)(-2)$

$= -2$ (gain of 2 electrons on the sulfur atom; reduction)

Example 12 Conversion: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2$

Reactants: C_6H_6 and HNO_3

Molecule	C_6H_6	HNO_3
mean ON	$6C + 6H = 0$	$1H + 1N + 3O = 0$
	$6C + 6(+1) = 0$	$1(+1) + 1N + 3(-2) = 0$
	$C = -1$	$N = +5$

Product: $C_6H_5NO_2 \rightarrow C_6H_5^{+} + {}^{-}NO_2$

Molecule	Organic fragment	Inorganic fragment
$C_6H_5NO_2$	$C_6H_5^{+}$	NO_2^{-}
mean ON	$6C + 5H = +1$	$1N + 2O = -1$
	$6C + 5(+1) = +1$	$1N + 2(-2) = -1$
	$C = -\frac{2}{3}$	$N = +3$

Δ mean ON$_C$ = mean ON$_C$ $(C_6H_5^{+})$ – mean ON$_C$ (C_6H_6)

$= \left(-\frac{2}{3}\right) - (-1)$

$= +\frac{1}{3}$ (oxidation occurring on the carbon atoms)

Δ mean ON$_N$ = mean ON$_N$ (NO_2^{-}) – mean ON$_N$ (HNO_3)

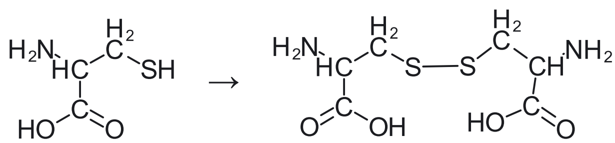
$= (+3) - (+5)$

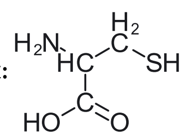
$= -2$ (reduction occurring on the nitrogen atom)

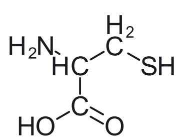
Te^- $= n_C\,\Delta$ mean ON_C
$= (6)\left(+\frac{1}{3}\right)$
$= +2$ (loss of 2 electrons on the carbon atoms; oxidation)

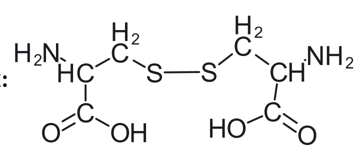
Te^- $= n_N\,\Delta$ mean ON_N
$= (1)\,(-2)$
$= -2$ (gain of 2 electrons on the nitrogen atom; reduction)

Example 13 Conversion: cysteine → cystine



Reactant:  $\rightarrow H_2N^- + HOOCCH^+CH_2^+ + {}^-SH$
$\rightarrow H_2N^- + C_3H_4O_2^{+2} + {}^-SH$

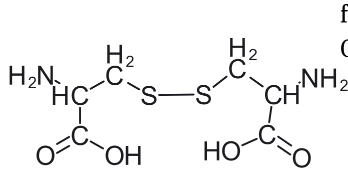
Molecule	Organic fragment	Inorganic fragment	Inorganic fragment
 Cysteine $C_3H_7O_2NS$	$C_3H_4O_2^{+2}$	NH_2^-	SH^-
mean ON	$3C + 4H + 2O = +2$	$1N + 2H = -1$	$1S + 1H = -1$
	$3C + 4(+1) + 2(-2) = +2$	$1N + 2(+1) = -1$	$1S + 1(+1) = -1$
	$C = +\frac{2}{3}$	$N = -3$	$S = -2$

Product: 

$\rightarrow HOOCCH^+CH_2^+ + NH_2^- + {}^-SS^- + NH_2^- + {}^+CH_2CH^+COOH$

$\rightarrow C_3H_4O_2^{+2} + NH_2^- + {}^-SS^- + NH_2^- + C_3H_4O_2^{+2}$

$\rightarrow C_6H_8O_4^{+4} + NH_2^- + S_2^{-2} + NH_2^-$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment	Inorganic fragment
 Cystine $C_6H_{12}O_4N_2S_2$	$C_6H_8O_4^{+4}$	NH_2^-	S_2^{-2}	NH_2^-
mean ON	$6C + 8H + 4O = +4$	$1N + 2H = -1$	$2S = -2$	$1N + 2H = -1$
	$6C + 8(+1) + 4(-2) = +4$	$1N + 2(+1) = -1$	$S = -1$	$1N + 2(+1) = -1$
	$C = +\frac{2}{3}$	$N = -3$		$N = -3$

Δ mean ONc = mean ONc $(C_6H_8O_4^{+4})$ – mean ONc $(C_3H_4O_2^{+2})$
$= \left(+\frac{2}{3}\right) - \left(+\frac{2}{3}\right)$
= 0 (non-redox reaction on the carbon atoms)

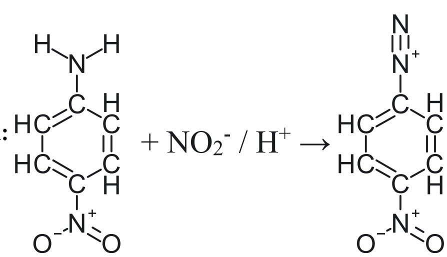
Δ mean ONn = mean ONn (NH_2^-) – mean ONn (NH_2^-)
= (–3) – (–3)
= 0 (non-redox reaction on the nitrogen atom)

Δ mean ONs = mean ONs (S_2^{-2}) – mean ONs (SH^-)
= (–1) – (–2)
= +1 (oxidation occurring on the sulfur atoms)

Te^- = ns Δ mean ONs
= (2) (+1)
= +2 (loss of 2 electrons on the sulfur atoms; oxidation)

In Example 13, Δ mean ONs > 0 represents there is a loss of electrons occurring on the sulfur atoms, but not occurring on the carbon atoms (Δ mean ONc = 0) nor the nitrogen atoms (Δ mean ONn = 0).

Example 14 Conversion:



$O_2NC_6H_4NH_2 + NO_2^-/H^+ \rightarrow O_2NC_6H_4{}^+N{\equiv}N$

Reactants: $O_2NC_6H_4NH_2$ and NO_2^-

$O_2NC_6H_4NH_2 \rightarrow O_2N^- + {}^+C_6H_4^+ + NH_2^-$
$\rightarrow NO_2^- + C_6H_4^{+2} + NH_2^-$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment	Reactant (ion)
$O_2NC_6H_4NH_2$	$C_6H_4{}^{+2}$	NO_2^-	NH_2^-	nitrite, NO_2^-
mean ON	6C + 4H = +2	1N + 2O = –1	1N + 2H = –1	1N + 2O = –1
	6C + 4(+1) = +2	1N + 2(–2) = –1	1N + 2(+1) = –1	1N + 2(–2) = –1
	$C = -\frac{1}{3}$	N = +3	N = –3	N = +3

Product: $O_2NC_6H_4{}^+N{\equiv}N$

$O_2NC_6H_4{}^+N{\equiv}N \rightarrow O_2N^- + {}^+C_6H_4^+ + N{\equiv}N$
$\rightarrow NO_2^- + C_6H_4^{+2} + N_2$

Molecule	Organic fragment	Inorganic fragment	Inorganic fragment
$O_2NC_6H_4{}^+N{\equiv}N$	$C_6H_4{}^{+2}$	NO_2^-	N≡N
mean ON	6C + 4H = +2	1N + 2O = –1	2N = 0
	6C + 4(+1) = +2	1N + 2(–2) = –1	N = 0
	$C = -\frac{1}{3}$	N = +3	

Δ mean ONc = mean ONc $(C_6H_4{}^{+2})$ – mean ONc $(C_6H_4{}^{+2})$
$= \left(-\frac{1}{3}\right) - \left(-\frac{1}{3}\right)$
= 0 (non-redox reaction occurring on the carbon atoms)

Δ mean ON_N = mean ON_N (NO_2^-) – mean ON_N (NO_2^-)
= (+3) – (+3)
= 0 (non-redox reaction occurring on the nitrogen atom in the nitro group)
Δ mean ON_N = mean ON_N ($\mathbf{N}\equiv N$) – mean ON_N ($\mathbf{N}H_2^-$)
= (0) – (–3)
= +3 (oxidation occurring on the nitrogen atom)
Δ mean ON_N = mean ON_N ($N\equiv\mathbf{N}$) – mean ON_N ($\mathbf{N}O_2^-$ from the reactant nitrite)
= (0) – (+3)
= –3 (reduction occurring on the nitrogen atom)
Te^- = n_N Δ mean ON_N ($O_2NC_6H_4\mathbf{N}H_2$ and NO_2^-/H^+ to $O_2NC_6H_4{}^+\mathbf{N}\equiv N$)
= (1) (+3)
= +3 (loss of 3 electrons on the nitrogen atom in the amino group; oxidation)
Te^- = n_N Δ mean ON_N ($O_2NC_6H_4NH_2$ and $\mathbf{N}O_2^-/H^+$ to $O_2NC_6H_4{}^+N\equiv\mathbf{N}$)
= (1) (–3)
= –3 (gain of 3 electrons on the nitrogen atom in the reactant nitrite; reduction)

In Example 14, Δ mean ON_C = 0 represents there is no gain or loss of electrons occurring on the carbon atoms in the hydrocarbon groups. Δ mean ON_N = 0 represents there is no gain or loss of electrons occurring on the nitrogen atoms in the nitro groups. The nitrogen atom of reactant nitrite ($\mathbf{N}O_2^-$) functions as oxidizing agent and the nitrogen atom of amino group ($R-\mathbf{N}H_2$) functions as reducing agent in forming organic diazonium cation ($R-{}^+\mathbf{N}\equiv\mathbf{N}$).

Conclusions

Oxidation number is an electron-counting concept for defining and balancing redox reactions. The ON for nitrogen and sulfur atoms can range from –3 to +5 and from –2 to +6 respectively. However, when the mean ON_C of ONC and OSC are counted in terms of their molecular formulas, the ON of nitrogen and sulfur atoms are assumed to be –3 and –2 respectively. This assumption will lead to the miscalculation of the mean organic ON_C. To overcome this limitation, this paper explores the bond-dividing method.

This method begins with the structural formulas of ONC and OSC. The carbon-sulfur and carbon-nitrogen bonds are then divided into organic and inorganic fragments. After dividing the bonds, a molecular formula of the organic fragment is resulted by summating all individual organic fragment's molecular formula. Lastly the mean oxidation numbers of carbon atoms, nitrogen atoms, and sulfur atoms can be calculated by the molecular formulas of their fragments.

Furthermore, when comparing ONC or OSC molecules in a redox conversion, changes of mean oxidation numbers of carbon atoms, nitrogen atoms, and sulfur atoms can be used as indicators for identifying the redox positions and determining the number of transferred electrons.

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