12-28-2021

Exploring the Relationships Among Stoichiometric Coefficients, Number of Transferred Electrons, Mean Oxidation Number of Carbons, and Oxidative Ratio in Organic Combustion reactions

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Research Article

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Exploring the relationships among stoichiometric coefficients, number of transferred electrons, mean oxidation number of carbons, and oxidative ratio in organic combustion reactions

https://doi.org/10.1515/cti-2021-0020
Received July 27, 2021; accepted December 11, 2021; published online December 28, 2021

Abstract: Combustion reactions, stoichiometry, and redox reactions are some of the basic contents in chemistry curriculum. Although the counting of transferred electrons is critical in redox reactions, assigning mean oxidation number of organic carbons (ONc) is not always easy. Even though the relationship between the oxidative ratio (OR) and ONc is known, the relationship between the number of transferred electrons (Te^-) and OR has not been thoroughly studied. The H-atom method has already been developed to balance and deduct organic combustion reactions. It can be used further to help establish the relationships among the stoichiometric coefficients (SC), the number of transferred hydrogens (TH), and Te^-. This article uses the procedures of the H-atom method for balancing and deducting, and the known relationships among SC, TH, and Te^- for exploring the relationships among SC, Te^-, ONc, and OR in organic combustion reactions. By integrating three sets of relationships: (i) SC and Te^-, (ii) Te^- and ON, and (iii) SC and OR, the interconversions among SC, Te^-, ONc, and OR can be mathematically formulated. Furthermore, Te^-, ONc, and OR can be assigned by SC and the general molecular formula of $C_xH_yO_zX_w$.

Keywords: mean oxidation number of organic carbons; molecular formula; number of transferred electrons; organic combustion reaction; oxidative ratio; stoichiometric coefficients.

Introduction

Combustion reactions, stoichiometry, and redox reactions are some of the basic contents in general chemistry curriculum (Chang & Goldsby, 2013; Tro, 2014). Redox reactions can be defined in four different models: electron transfer, H-atom transfer, O-atom transfer, and oxidation number (IUPAC, 2019). Oxidation number is an electron-counting concept (IUPAC, 2019; Karen, McArdle & Takats, 2014, 2016) for balancing redox reactions. It is counted by using chemical formula methods (Bentley, Franzen & Chasteen, 2002; Halkides, 2000; Jurowski, Krzeczkowska & Jurowska, 2015; Kauffman, 1986). Although counting oxidation number is critical for balancing organic redox reactions, assigning oxidation number of organic carbons is not always easy.

The mean oxidation number of organic carbons (or the mean oxidation state of organic carbons; ONc) is used as a redox indicator in the fields of ecosystem (Masiello, Gallagher, Randerson, Deco & Chadwick, 2008),

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environmental chemistry (Kroll et al., 2011), geochemistry (Dick & Shock, 2011), and water biochemical treatment (Li et al., 2018).

Oxidative ratio (OR) is a reaction-based parameter which is defined by the ratio of the number of moles of O_2 to one mole of CO_2 in a chemical reaction (Hockaday et al., 2015; Worrall, Clay, Masiello & Mynheer, 2013). The relationship between OR and ONc has already been known (Hockaday et al., 2015; Masiello et al., 2008; Worrall, Clay, Masiello & Mynheer, 2013). OR is a macroscopic concept which can be determined by the stoichiometric coefficients (SC) of an overall balanced combustion equation. ONc is a microscopic concept which can be used for counting the number of transferred electrons (Te^-). Although an organic combustion reaction is an electron transfer reaction, the relationships among Te^-, ONc, and OR have not been revealed. The H-atom method (Yuen & Lau, 2021) has been developed to balance and deduct organic combustion reactions, and has also been used to establish the relationships among SC, the number of transferred hydrogens (TH), and Te^- in organic combustion reactions. This article applies the procedures of the H-atom method for balancing and deducting, and the known relationships among SC, TH and Te^- for exploring the relationships among the SC, Te^-, ONc, and OR in organic combustion reactions. An organic compound containing the general chemical formula of $C_xH_yO_zX_w$ is chosen as an exemplar.

By integrating three sets of relationships: (i) SC and Te^-, (ii) Te^- and ONc in a half combustion reaction, and (iii) SC and OR in an overall combustion reaction, the interconversions among these four parameters can be demonstrated by using the H-atom method.

Assigning Te^- and ONc in a half combustion reaction

By using the organic compound, CCl_3COOH, which contains halogen and oxygen atoms, as an example, the H-atom method shows how Te^- is counted. Then ONc is assigned by the derived mathematical formula.

Example 1: Balancing a half combustion reaction of CCl_3COOH.

$C_2HO_2Cl_3 \rightarrow CO_2 + HCl$
$C_2HO_2Cl_3 \rightarrow 2CO_2 + 3HCl$
$C_2HO_2Cl_3 + 2H + 2O \rightarrow 2CO_2 + 3HCl$
$C_2HO_2Cl_3 + 2H + 2O + 2H \rightarrow 2CO_2 + 3HCl + 2H$
$C_2HO_2Cl_3 + 2H_2O \rightarrow 2CO_2 + 3HCl + 2H$

The above balanced half reaction shows that there are two carbon atoms (nc = 2) involved in the oxidation reaction. That means there is either a loss of two H atoms (TH = +2) or a loss of two protons and two electrons ($2H \rightarrow 2H^+ + 2e^-$; $Te^- = +2$).

The relationship between the change of mean oxidation number of organic carbons (ΔONc) and Te^- is established in a half redox reaction (Yuen & Lau, 2022). Then by deducting the mathematical equations, ONc can be assigned by Te^-.

$$Te^- = nc\,\Delta ONc$$

$$\Delta ONc = ONc\,(CO_2) - ONc\,(C_2HO_2Cl_3)$$

$$ONc\,(C_2HO_2Cl_3) = ONc\,(CO_2) - \frac{Te^-}{nc}$$

$$ONc\,(CO_2) = +4;\ Te^- = +2;\ nc = 2$$

$$\begin{aligned} \mathrm{ONc}\,(C_2HO_2Cl_3) &= \mathrm{ONc}\,(CO_2) - \frac{Te^-}{nc} \\ &= 4 - \frac{(+2)}{2} \\ &= +3 \end{aligned}$$

The calculated ONc of $C_2HO_2Cl_3$ is equal to +3.

Counting OR in an overall combustion reaction

The H-atom method can balance an overall organic combustion reaction and consequently count OR.

Example 2: Balancing an overall organic combustion reaction of "$C_2HO_2Cl_3 + O_2 \rightarrow CO_2 + H_2O + HCl$".

Step 1.	$C_2HO_2Cl_3 \rightarrow CO_2 + HCl$
	$O_2 \rightarrow H_2O$
Step 2.	$C_2HO_2Cl_3 + 2H_2O \rightarrow 2CO_2 + 3HCl + 2H$ (from Example 1)
	$O_2 + 4H \rightarrow 2H_2O$
Step 3.	$(C_2HO_2Cl_3 + 2H_2O \rightarrow 2CO_2 + 3HCl + 2H) \times 2$
	$(O_2 + 4H \rightarrow 2H_2O) \times 1$
Step 4.	$2C_2HO_2Cl_3 + 4H_2O + O_2 + 4H \rightarrow 4CO_2 + 6HCl + 4H + 2H_2O$
Step 5.	$2C_2HO_2Cl_3 + 2H_2O + O_2 \rightarrow 4CO_2 + 6HCl$

According to the above reaction, the OR which goes through the combustion of $C_2HO_2Cl_3$ can be counted by the molar ratio of oxygen gas to carbon dioxide.

$$nO_2 = 1; nCO_2 = 4$$

$$\begin{aligned} OR &= \frac{nO_2}{nCO_2} \\ &= \frac{1}{4} \end{aligned}$$

Deducting relationship between SC and Te^- in a half combustion reaction

To deduct the stoichiometric relationship between SC and Te^- in a half oxidation combustion reaction, a general molecular formula of $C_xH_yO_zX_w$ is chosen to demonstrate the operating procedures.

Example 3: Given $C_xH_yO_zX_w \rightarrow CO_2 + HX$.

$C_xH_yO_zX_w + (2x - z)O \rightarrow xCO_2 + wHX + (y - w)H$
$C_xH_yO_zX_w + (2x - z)O + 2(2x - z)H \rightarrow xCO_2 + wHX + (y - w)H + 2(2x - z)H$
$C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H$

$C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H$
$(4x + y - 2z - w)H \rightarrow (4x + y - 2z - w)H^+ + (4x + y - 2z - w)e^-$
$C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H^+ + (4x + y - 2z - w)e^-$

Regarding $C_xH_yO_zX_w$, the x number of carbons (nc = x) has participated. TH is equal to Te^- ($TH = Te^-$) and Te^- are lost ($Te^- > 0$) in the half oxidation reaction.

$$TH = 4x + y - 2z - w$$

$$Te^- = 4x + y - 2z - w$$

Deriving relationships among SC, Te⁻, and ONc

According to the relationship between SC and Te^-, to complement the mathematical equation of $Te^- = nc\,\Delta ONc$, the relationship between SC and ONc of $C_xH_yO_zX_w$ is shown. The triangular relationships among SC, Te^-, and ONc are established in a half redox reaction and exhibited in Figure 1.

$$Te^- = nc\,\Delta ONc$$

$$\Delta ONc = \frac{Te^-}{nc}$$

$$\Delta ONc = ONc\,(\text{product}) - ONc\,(\text{reactant})$$

For the balanced half oxidation reaction:

$$C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H$$

$$Te^- = (4x + y - 2z - w)\,;\; nc = x$$

$$\Delta ONc = \frac{Te^-}{nc}$$

$$\Delta ONc = \frac{4x + y - 2z - w}{x}$$

$$\Delta ONc = ONc\,(\text{product}) - ONc\,(\text{reactant})$$

$$\Delta ONc = ONc\,(CO_2) - ONc\,(C_xH_yO_zX_w)$$

$$ONc\,(C_xH_yO_zX_w) = ONc\,(CO_2) - \Delta ONc$$

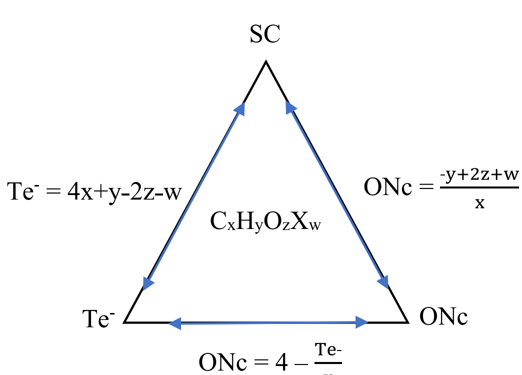

Figure 1: Triangular relationships among SC, Te^-, and ONc in a half redox reaction.

$$ONc(C_xH_yO_zX_w) = ONc(CO_2) - \frac{Te^-}{nc}$$
$$= 4 - \frac{Te^-}{x}$$
$$= 4 - \frac{4x + y - 2z - w}{x}$$
$$= \frac{-y + 2z + w}{x}$$

Deriving relationships among SC, OR, and ONc

The stoichiometric relationship between SC and ONc of $C_xH_yO_zX_w$ is deducted by balancing two half reactions. Then the stoichiometric relationship between SC and OR is derived by the balancing overall combustion.

$$nO_2 = \frac{4x + y - 2z - w}{4};\ nCO_2 = nc = x$$

$$OR = \frac{nO_2}{nCO_2}$$
$$= \frac{4x + y - 2z - w}{4x}$$

Example 4: Given $C_xH_yO_zX_w + O_2 \rightarrow CO_2 + H_2O + HX$.

Step 1.	$C_xH_yO_zX_w \rightarrow CO_2 + HX$ $O_2 \rightarrow H_2O$
Step 2.	$C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H$ (from Example 3) $O_2 + 4H \rightarrow 2H_2O$
Step 3.	$(C_xH_yO_zX_w + (2x - z)H_2O \rightarrow xCO_2 + wHX + (4x + y - 2z - w)H) \times 4$ $(O_2 + 4H \rightarrow 2H_2O) \times (4x + y - 2z - w)$
Step 4.	$4C_xH_yO_zX_w + 4(2x - z)H_2O + (4x + y - 2z - w)O_2 + 4(4x + y - 2z - w)H$ $\rightarrow 4xCO_2 + 4wHX + 4(4x + y - 2z - w)H + 2(4x + y - 2z - w)H_2O$
Step 5.	$4C_xH_yO_zX_w + (4x + y - 2z - w)O_2 \rightarrow 4xCO_2 + 4wHX + 2(y - w)H_2O$ $C_xH_yO_zX_w + \frac{4x+y-2z-w}{4}O_2 \rightarrow xCO_2 + \frac{y-w}{2}H_2O + wHX$

Based on the relationship of $ONc = \frac{-y+2z+w}{x}$ which is derived from the balanced half reactions and $OR = \frac{4x+y-2z-w}{4x}$ which is derived from the balanced overall reaction, the relationship of $OR = 1 - \frac{ONc}{4}$ can be derived correspondingly. The relationships among SC, OR, and ONc for $C_xH_yO_zX_w$ are shown in Figure 2.

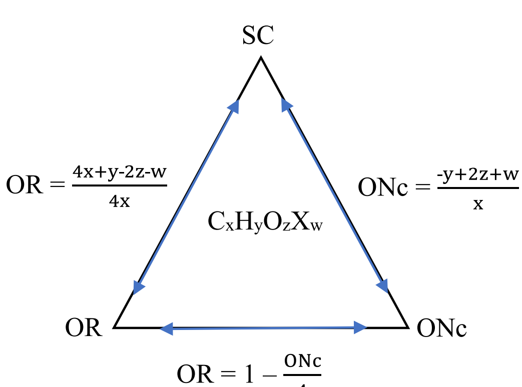

Figure 2: Triangular relationships among SC, OR, and ONc in an overall redox reaction.

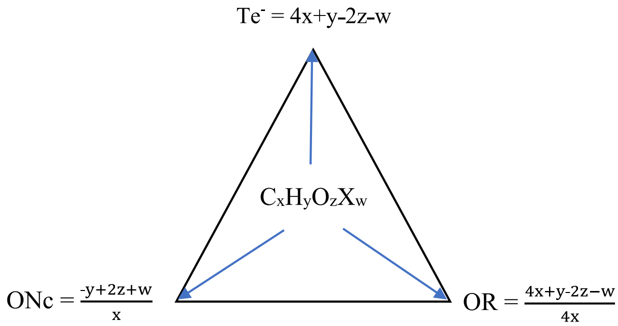

Figure 3: From molecular formula to counting Te^{-}, ONc, and OR.

From molecular formula to counting Te^{-}, ONc, and OR

Based on the general molecular formula of $C_xH_yO_zX_w$, the relationships among SC, Te^{-}, and ONc in a half reaction and the relationships among SC, OR, and ONc in an overall reaction are integrated. Then the established mathematical formulas and triangular relationships are shown in Figure 3.

Te^{-}, ONc, and OR can be assigned by SC and the given chemical formula of $C_xH_yO_zX_w$. An example is shown below.

Example 5: Determining Te^{-}, ONc, and OR of CCl_3COOH in a combustion reaction.

When comparing CCl_3COOH ($C_2HO_2Cl_3$) to $C_xH_yO_zX_w$, x = 2; y = 1; z = 2; w = 3

$Te^{-} = 4x + y - 2z - w$	$ONc = \frac{-y + 2z + w}{x}$	$OR = \frac{4x + y - 2z - w}{4x}$
$= 4(2) + (1) - 2(2) - (3)$	$= \frac{-(1) + 2(2) + (3)}{2}$	$= \frac{4(2) + (1) - 2(2) - (3)}{4(2)}$
$= +2$	$= +3$	$= \frac{1}{4}$

To determine Te^{-}, ONc, and OR of the CCl_3COOH compound, the H-atom balancing equations method has been applied in Example 1 and Example 2, and the molecular formula method has been applied in Example 5. In comparison, Te^{-}, ONc, and OR can be counted by a given molecular formula effectively in Example 5.

Interconversions among SC, Te^{-}, ONc, and OR

By combining the half reaction to an overall organic combustion reaction, the relationships among SC, Te^{-}, ONc, and OR can be derived accordingly. The interconversions are summarized in Table 1 and graphically demonstrated in Figure 4.

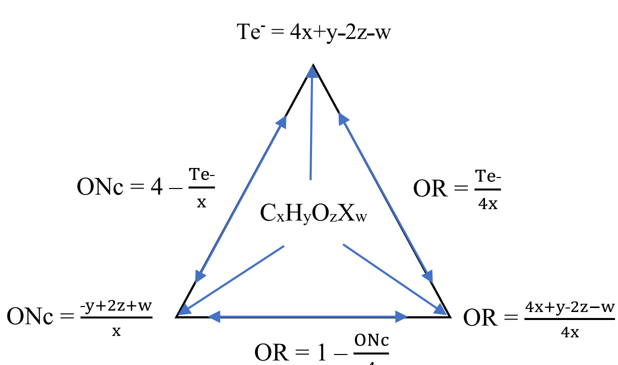

Figure 4: Interconversions among SC, Te^{-}, ONc, and OR.

Table 1: Mathematical relationships among Te^-, ONc, and OR in organic combustion reactions.

Te^- and ONc	Te^- and OR	ONc and OR
nc = x	$nCO_2 = nc = x$	$OR = \frac{Te^-}{4x}$
$ONc = 4 - \frac{Te^-}{nc}$	$nO_2 = \frac{Te^-}{4}$	$ONc = 4 - \frac{Te^-}{x}$
$ONc = 4 - \frac{Te^-}{x}$	$OR = \frac{nO_2}{nCO_2}$	$\frac{ONc}{4} = 1 - \frac{Te^-}{4x}$
$Te^- = x\,(4 - ONc)$	$OR = \frac{Te^-}{4x}$	$ONc = 4\,(1 - OR)$
	$Te^- = 4x\,(OR)$	$OR = 1 - \frac{ONc}{4}$

Based on the given molecular formula of $C_xH_yO_zX_w$, the OR can be calculated by using SC, Te^-, or ONc. Examples are shown below.

Example 6: Determining Te^-, ONc, and OR of C_6H_5COCl in a combustion reaction.

When comparing C_6H_5COCl (C_7H_5OCl) to $C_xH_yO_zX_w$, x = 7; y = 5; z = 1; w = 1

By using x, y, z, w →

$$Te^- = 4x + y - 2z - w = 4(7) + (5) - 2(1) - (1) = +30$$

$$ONc = \frac{-y + 2z + w}{x} = \frac{-(5) + 2(1) + (1)}{7} = -\frac{2}{7}$$

$$OR = \frac{4x + y - 2z - w}{4x} = \frac{4(7) + (5) - 2(1) - (1)}{4(7)} = \frac{15}{14}$$

By using Te^- →

$$ONc = 4 - \frac{Te^-}{x} = 4 - \frac{(+30)}{7} = -\frac{2}{7}$$

$$OR = \frac{Te^-}{4x} = \frac{(+30)}{4(7)} = \frac{15}{14}$$

By using ONc →

$$OR = 1 - \frac{ONc}{4} = 1 - \left(-\frac{2}{7} \times \frac{1}{4}\right) = \frac{15}{14}$$

Example 7: Determining Te^-, ONc, and OR of CH_3COOH in the combustion reaction.

When comparing CH_3COOH ($C_2H_4O_2$) to $C_xH_yO_zX_w$, x = 2; y = 4; z = 2; w = 0

By using x, y, z, w →

$$Te^- = 4x + y - 2z - w = 4(2) + (4) - 2(2) - (0) = +8$$

$$ONc = \frac{-y + 2z + w}{x} = \frac{-(4) + 2(2) + (0)}{2} = 0$$

$$OR = \frac{4x + y - 2z - w}{4x} = \frac{4(2) + (4) - 2(2) - (0)}{4(2)} = 1$$

By using Te^- →

$$ONc = 4 - \frac{Te^-}{x} = 4 - \frac{(+8)}{2} = 0$$

$$OR = \frac{Te^-}{4x} = \frac{(+8)}{4(2)} = 1$$

By using ONc →

$$OR = 1 - \frac{ONc}{4} = 1 - 0 = 1$$

Conclusions

In this article, a reaction-based approach is explored to establish the relationships among SC, Te^-, ONc, and OR in organic combustion reactions by using the H-atom method. Firstly, the triangular relationships among SC, Te^-, and ONc are derived in the half organic combustion reaction. Secondly, the relationships among SC, OR, and ONc are revealed in the overall organic combustion reaction. Then the interconversions among SC, ONc, OR, and Te^- are established and mathematically formulated. Furthermore, Te^-, ONc, and OR are counted by using SC as well as the general molecular formula of $C_xH_yO_zX_w$.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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