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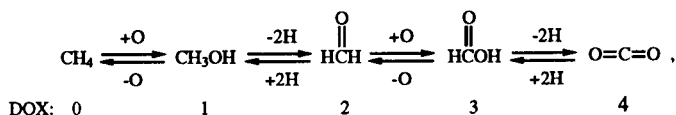
The degree of oxidation (DOX) of an organic compound  $C_nH_mE_p$ , where E is any one or more of eleven elements more electronegative than hydrogen, is defined with respect to an alkane  $C_nH_{2n+2}$  (DOX = 0) as a reference. One can calculate DOX either from the molecular or the structural formula of the compound by the relationship  $DOX = DU + p$ , where DU is the degree of unsaturation (*i.e.* index of hydrogen deficiency) in the molecule. The concept is developed for E is oxygen, and is extended to other chalcogens, as well as to halogens, nitrogen, phosphorus, and arsenic. Particular examples of heterocyclic compounds are considered. It is noted that addition of a simple hydride of E to an organic compound or elimination of the hydride from  $C_nH_mE_p$  leaves DOX unchanged.

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## Introduction.

In organic chemistry the traditional definition of oxidation is the addition of oxygen to a molecule or the removal of hydrogen from it. Reduction is then a reverse process. Apparently, no one has yet proposed a procedure whereby one can assign a numerical value to the oxidation state, *i.e.* the degree of oxidation (abbreviated DOX in this article), of an organic molecule in general. It is the goal of this paper to show that one can quantify DOX in terms of an integral value which can be obtained from observation of *either* the molecular or the structural formula of the compound. Moreover, DOX has the desirable characteristic of increasing in size with increasing extent of oxidation of a molecule.

In the simplest organic redox series of one carbon atom per molecule we have



where proceeding from left to right is oxidation and from right to left is reduction. Using methane as a reference compound (DOX assigned as zero) one can represent each successive oxidative step of either adding one oxygen atom to the molecule or of removing two hydrogen atoms from the molecule as increasing DOX by one unit. Carey presented this numerical measure of DOX in terms of the number of carbon-oxygen bonds found in the molecule [1], while Campbell and Ali obtained the same values by counting the number of H atoms in methane which must be replaced by OH groups (with accompanying loss of  $H_2O$  for cases where two OH groups are attached to the same carbon atom) in order to produce the molecule being considered [2].

Several authors have extended the concept of oxidation to include the process of increasing the nitrogen or halogen content of an organic molecule [3-5], or, more broadly, of increasing the content of any element more electronegative than carbon [6-8]. However, since we will choose alkanes as reference compounds, oxidation ought to be defined as increasing the content of any element more electronegative than hydrogen, as suggested by Haines [5]. The Haines concept is adopted in this paper.

Values of electronegativity for elements have been defined in various ways [9]. However, for this paper we select as oxidizing elements only the representative or main-group non-metals which occur in periodic groups VA, VIA, and VIIA and which have electronegativities greater than that of hydrogen on the Mulliken-Jaffe scale [9]. This list contains nitrogen, phosphorus, and arsenic of group VA, oxygen, sulfur, selenium, and tellurium of group VIA, and fluorine, chlorine, bromine, and iodine of group VIIA, *i.e.* eleven elements in all. Of these elements the first seven are of special interest as heteroatoms in rings, while all of them occur in functional groups and form simple hydrides.

## Rules for Calculation of DOX.

Let us consider a compound *B* of molecular formula  $C_nH_mE_p$ , where E is any of the qualified electronegative elements noted above or a combination of those elements (*p* atoms total). We choose as a standard of reference the corresponding alkane *A*,  $C_nH_{2n+2}$  (the parent hydrocarbon for *B*), to which we assign DOX = 0. Going from *A* to *B* will, in general, involve two processes, *viz.* (i) removal of a number of  $H_2$  units from *A* to give the unsaturation equivalent to that in *B*, plus (ii) addition of *p* atoms of E to this unsaturated core. The number of  $H_2$  units removed in item (i) is defined as the index of hydrogen deficiency or (as used here) the degrees of unsaturation (DU) of *B*. As one can see in the preceding stepwise transformation

of methane→carbon dioxide the DOX value at each stage is given by the sum of the double bonds in the molecule (*i.e.* DU) and the number of oxygen atoms in the molecule (*i.e.* *p*). In general, we now define DOX in this same way for any organic molecule  $C_nH_mE_p$ , thus:

$$\text{DOX} = \text{DU} + p$$

Since one can determine the values of DU and *p* for *B* from its molecular formula, one can easily also obtain the value of DOX for *B* in this manner.

In a previous publication Klemm enumerated the rules for calculating DU and illustrated using this value in structural studies [10]. Briefly, the calculation involves the initial determination of the molecular formula of a hydrocarbon, *Z*, which has the same degree of unsaturation as is present in *B*. *Z* is called the "equivalent hydrocarbon." One accomplishes the transformation  $B \rightarrow Z$  as follows (rules applied consecutively in any order):

1. Replace all halogen atoms (*i.e.* monovalent atoms of Group VIIA) by an equal number of H atoms in the formula.

2. Delete all divalent atoms (*i.e.* O, S, Se, Te of Group VIA) from the formula.

3. Delete all trivalent atoms (*i.e.* N, P, As of Group VA) from the formula as units YH, where Y is the trivalent atom. Then *Z* is the resultant equivalent hydrocarbon  $C_nH_q$ . One calculates DU from the formula

$$\text{DU} = \frac{2n + 2 - q}{2} = n + 1 - 1/2 q$$

As an example, assume *B* has the formula  $C_8H_8ClNO_2S$ . By Rule 1 one obtains  $B \Leftrightarrow C_8H_9NO_2S$ , where the symbol " $\Leftrightarrow$ " is read "is equivalent to." By Rule 2,  $C_8H_9NO_2S \Leftrightarrow C_8H_9N$ . Then from Rule 3 one gets  $Z = C_8H_8$ , and  $\text{DU} = 8 + 1 - 4 = 5$ . Also  $\text{DOX} = 5 + 5 = 10$ .

Following are five hypothetical structures (of a very large number of possibilities) which would fit these qualifications for *B*. One notes that certain conventions must

be followed in order to correlate DOX values and structural formulas with each other. They are given here [11].

a. Aromatic rings are drawn with double and single bonds, not with internal circles. Both the ring ( $\text{DU} = 1$ ) and the double bonds therein ( $\text{DU} = 1$  for each) are counted.

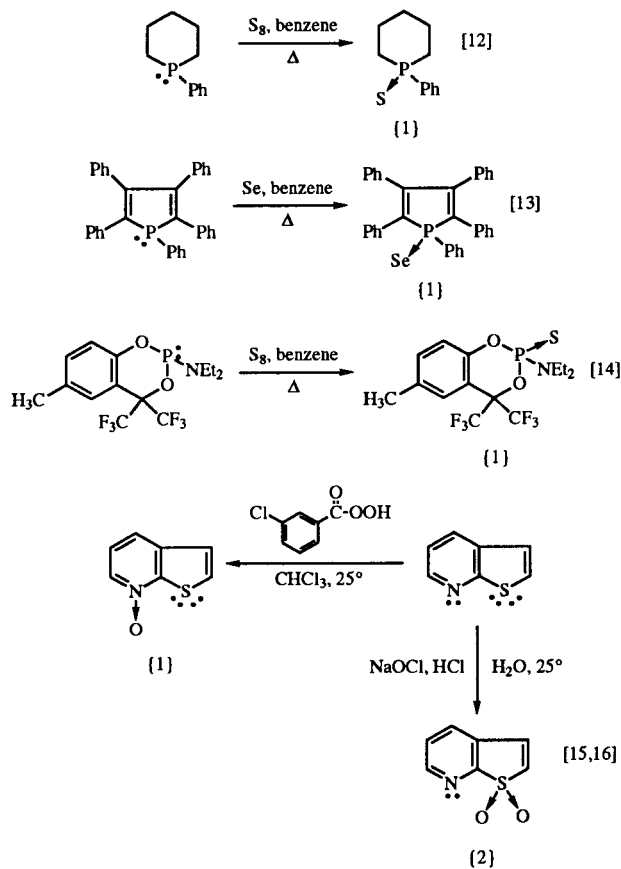
b. A chelate ring has  $\text{DU} = 0$ .

c. Tricovalencies for atoms in Group VA are maintained constant regardless of any changes in the ON values assigned to these atoms. To ensure this situation, coordinate covalent (also called dative or semipolar) bonds are introduced appropriately (see part d). Quaternary salts are treated as molecular compounds [11].

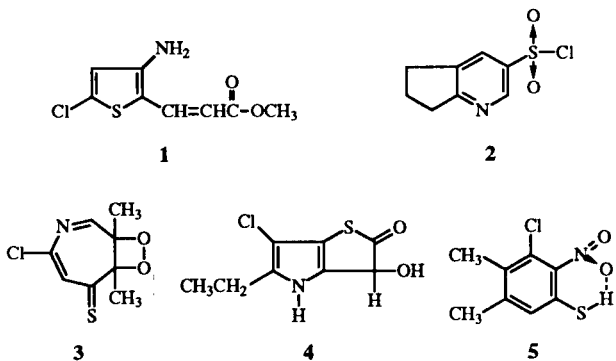
d. A coordinate covalent bond is represented by an arrow pointing from the electron-pair donating atom (of Group VA or VIA) to the electron-pair accepting atom (of Group VIA only). This bond has a DU count of zero, *i.e.* the acceptor atom is not considered to be divalent.

Some reactions which produce coordinate covalent bonds are shown in Scheme 1, where regioselectivity is observed in some cases.

Scheme 1 [a]



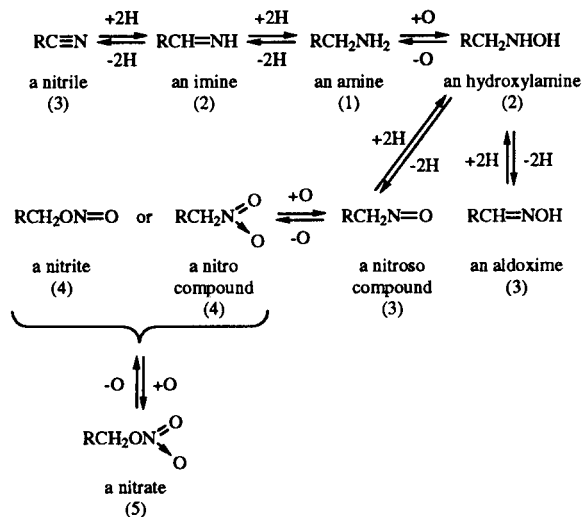
[a] Numbers in braces represent  $\Delta\text{DOX}$  values for formation of the product from its precursor.



## A Distinction Between Oxidation Number (ON) and DOX.

As regularly used an oxidation number (abbreviated ON here) refers to an individual atom in a molecule. It measures the capacity which the atom is showing in that

Scheme 2 [a]

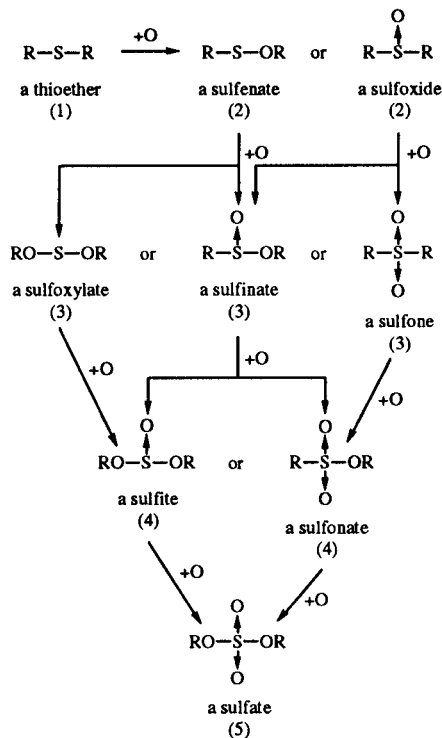


[a] Numbers in parentheses are DOX values. The transformations are hypothetical. They may or may not involve known experimental processes.

molecule toward bonding with atoms *more electronegative* than itself. In the simple cases of methane, carbon monoxide, and carbon dioxide one has ON values of -4, +2, and +4 for carbon. The negative ON for carbon in methane indicates that hydrogen is *less electronegative* than carbon. In slightly more complex organic molecules such as 2-hydroxypropanoic acid each carbon will have a different ON [17], but, nonetheless, the summation of the ON values in any molecule is taken as zero. In contrast, DOX is a measure of the state of oxidation of the whole molecule. For a molecule with  $n$  carbon atoms DOX is only zero for the reference alkane,  $\text{C}_n\text{H}_{2n+2}$ .

Schemes 2 and 3 illustrate systematic changes in DOX values for a primary amine and a thioether, respectively, as one alters oxidation-reduction at the heteroatom by changing its bonding to oxygen or hydrogen. Significant aspects of the Schemes are that one easily observes compounds which have the same DOX value, *e.g.* (a) a sulfoxylate, a sulfinate, and a sulfone, (b) a nitrite, a nitro compound, a sulfite, and a sulfonate, (c) an imine and an hydroxylamine, and (d) a nitrile, a nitroso compound, and an aldoxime. Relationships (c) and (d) will be discussed further in the next section.

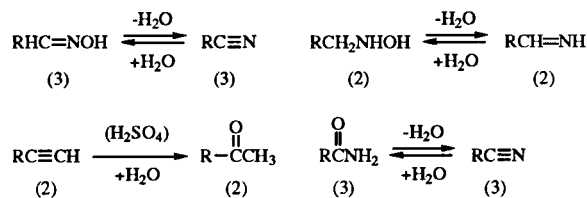
Scheme 3 [a]



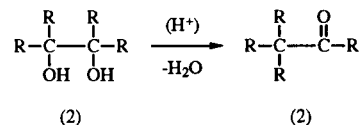
[a] See footnote in Scheme 2. For clarity, deoxygenation processes are not shown.

Scheme 4 [a]

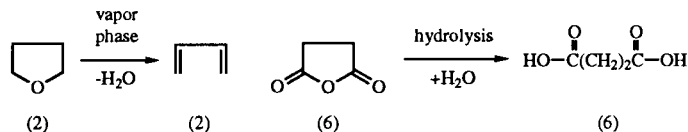
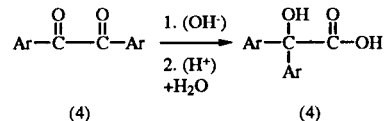
Constancy of DOX Values in Hydration-Dehydration Processes



The pinacol rearrangement is given by

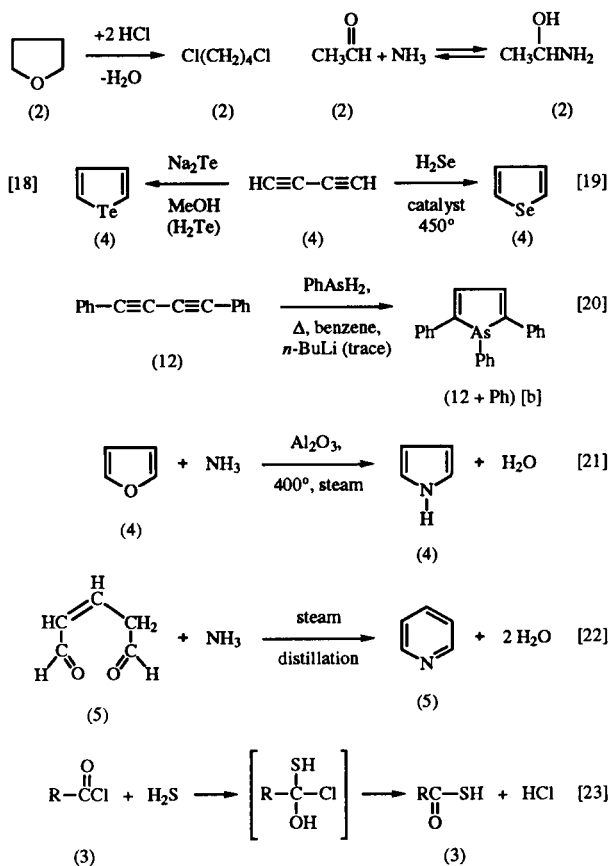


The benzoic acid rearrangement is shown as



[a] Numbers in parentheses are DOX values.

Scheme 5 [a]

Miscellaneous Reactions with  $\Delta\text{DOX} = 0$ 

[a] See footnote in Scheme 4. [b] Note that phenylarsine is a reactant, instead of arsine itself.

### Addition or Elimination Reactions of E Hydrides.

Water is an oxidatively neutral molecule, since it consists of a two-hydrogen reductive unit and a one-oxygen oxidative unit. For this reason addition of a water molecule to an organic molecule (or the elimination of a water molecule from the organic molecule) will leave the DOX value unchanged, *i.e.*  $\Delta\text{DOX} = 0$  for the reaction. A number of examples of these hydration-dehydration interconversions, including two from Scheme 2, are shown in Scheme 4. In fact, each electronegative element E has an hydride (HX for the halogens,  $\text{H}_2\text{G}$  for the chalcogens, and  $\text{YH}_3$  for the elements in Group VA) which are also oxidatively neutral and will act analogously (Scheme 5).

### Conclusion.

A broadened definition of oxidation-reduction in organic chemistry has been elaborated and a numerical measure of the degree of oxidation (DOX) of a molecule has been defined. DOX is calculable either from a molecular formula or from a structural formula. Examples of the relationships between various oxidized molecules are presented.

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