A study of correlation of the order of chemical reactivity of a sequence of binary compounds of nitrogen and oxygen in terms of frontier orbital theory

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The order of stability and chemical reactivity of a sequence of nine compounds of nitrogen and oxygen have been correlated in terms of the energies of the frontier orbitals. The order of stability has been correlated in terms of the height of the energy gap between the highest occupied molecular orbital and lowest occupied molecular orbital and the global hardness of the molecules while the order of chemical reactivity has been correlated in terms of their global softness.

NITROGEN and oxygen form a number of binary combination products called oxides of nitrogen and as many as nine such oxides, viz. N₂O, N₂O₃, N₂O₄, N₂O₅, NO₃⁻, NO₂⁻, NO⁻, NO₂⁺ and NO⁺ are known. The compounds are widely divergent in thermodynamic stability and chemical reactivity. Text books usually draw and discuss the electronic structure of such molecules invoking qualitative LCAO-MO theory, valence bond theory and the theory of n-center bonding. The electronic structures drawn in terms of such theories of bonding and chemical reactivities of such molecules are shown in Table 1. From a careful study of the electronic structures and chemical response of the molecules from the available source materials⁵, the molecules can be arranged in a sequence of increasing or decreasing order of thermodynamic stabilities and chemical reactivities. The chemical reactivity order or the order of response of the molecules towards attacking reagents may be arranged as follows:

\[ \text{NO}^+ < \text{NO}_3^- < \text{NO}_2^+ < \text{NO}_2^- < \text{NO}^- < \text{N}_2\text{O}_3 < \text{N}_2\text{O} < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5 \text{; order of chemical response.} \]

The order of thermodynamic stabilities of the molecules is just the reverse of the above sequence.

\[ \text{N}_2\text{O}_5 < \text{N}_2\text{O}_4 < \text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{NO}^- < \text{NO}_3^- < \text{NO}_2^+ < \text{NO}^+ \text{; order of thermodynamic stability.} \]

The intrinsic chemical reactivity or inertness and the inherent thermodynamic stability of molecules are not straightforward and evident in terms of electronic structures drawn in terms of the above mentioned theories of bonding as shown in Table 1. The relative thermodynamic stabilities and chemical response of different molecules are hardly intelligible in terms of such electronic structures.

But a study of the energies and symmetry types of a pair of frontier orbitals of molecules, within the framework of Self-Consistent Field Molecular Orbital Theory⁸, may furnish reliable and quantitative data for a straightforward prediction and comparative study of chemical and thermodynamic stabilities of molecules. The highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of a molecule are called the frontier orbitals. It was Fukui¹⁰ who first noticed the prominent role played by HOMO and LUMO in governing chemical reactions. It has been revealed by recent investigation that the gap in energy between the HOMO and LUMO is an important stability index¹⁰-¹². A large gap implies high stability and small gap implies low stability. The high stability in turn indicates low chemical reactivity and small gap indicates high chemical reactivity. The energy and symmetry type of, and the charge distribution in HOMO, and the energy and symmetry type of LUMO are known to determine the structures¹³⁻¹⁵ of molecules. The energy and symmetry types of such frontier orbitals are also found to be the principal factor for determining the occurrence and non-occurrence of chemical reactions and stereo-selective path in intra- and inter-molecular processes¹⁶.

Another very useful theory of electronic structure and reactivity of molecules involving the single pair of frontier orbitals is the Hard–Soft Acid Base (HSAB) principle of Pearson¹⁷. The work of Parr, Pearson and others¹¹,¹⁸⁻²⁶ within the framework of Density Functional Theory (DFT), has established a general rule predicting the stability of the electronic structure of molecules. The general rule of this new paradigm is that the index of chemical reactivity and stability of a molecule is its global hardness, \( \eta \). Increase in hardness increases the movement of the system towards a more stable configuration and when a chemical species moves away from its equilibrium configuration its hardness value decreases. When a system evolves towards a state of greater hardness, its stability increases. When a system evolves towards the state of lower hardness, its stability decreases. \( \eta \) is again used as an index of chemical reactivity. The higher the value of \( \eta \), the lesser is its reactivity. The global softness, \( S \), the inverse concept of hardness, is useful for a straightforward prediction of chemical reactivity. The soft molecules undergo changes in electron density more easily than the hard molecules and are more reactive than the hard molecules. A molecule having higher \( S \) value is more reactive than a molecule having smaller \( S \) value. In general, it can be said that the increase in softness increases chemical reactivity and increase in hardness decreases chemical reactivity.
It is, therefore, quite evident that the quantum chemical quantities—the HOMO–LUMO gap, the global hardness and the global softness can be used for a quantitative prediction of intrinsic stability, chemical reactivity as well as the relative stabilities and chemical reactivities of molecules. By comparative analysis of the computed values of $\Delta\varepsilon$, $\eta$ and $S$ of a series of molecules, one can arrange the molecules in a sequence of increasing or decreasing order of chemical reactivity and thermodynamic stability. The global hardness and the global softness are conventionally computed through frontier orbitals with the help of Koopmans' theorem. The $\Delta\varepsilon$ is simply obtained from the energies of the frontier orbitals.

The symmetry types and the energies of the frontier orbitals of each of the molecules are computed at their experimental geometry by invoking the CNDO/2 level Self-Consistent Field Molecular Orbital method of Pople and co-workers. The STO basis set and standard parameters are used in this calculation. The desired
Table 2. Symmetry types, energies, height of gap between energies of the HOMO and LUMO global hardness and global softness of the molecules

<table>
<thead>
<tr>
<th>Chemical systems</th>
<th>HOMO Symmetry type</th>
<th>Energy (ε_HOMO) a.u.</th>
<th>LUMO Symmetry type</th>
<th>Energy (ε_LUMO) a.u.</th>
<th>(ε_LUMO - ε_HOMO) (Δε) a.u.</th>
<th>Global hardness (η) a.u.</th>
<th>Global softness (S) a.u.^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO⁺</td>
<td>σ⁺</td>
<td>-1.3579</td>
<td>π</td>
<td>-0.4178</td>
<td>0.9401</td>
<td>0.4700</td>
<td>2.1276</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>ε'</td>
<td>-0.1961</td>
<td>a₁''</td>
<td>0.4754</td>
<td>0.6715</td>
<td>0.3357</td>
<td>2.9788</td>
</tr>
<tr>
<td>NO₂⁺</td>
<td>σ⁺</td>
<td>-1.0658</td>
<td>σ⁺</td>
<td>0.4062</td>
<td>0.6596</td>
<td>0.3298</td>
<td>3.0321</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>a₁</td>
<td>-0.0703</td>
<td>a₁</td>
<td>0.5519</td>
<td>0.6222</td>
<td>0.3111</td>
<td>3.2144</td>
</tr>
<tr>
<td>NO</td>
<td>σ⁺</td>
<td>0.0881</td>
<td>σ⁺</td>
<td>0.6817</td>
<td>0.5936</td>
<td>0.2968</td>
<td>3.3693</td>
</tr>
<tr>
<td>N₂O₃</td>
<td>a₁</td>
<td>-0.5074</td>
<td>a₁</td>
<td>0.0167</td>
<td>0.5241</td>
<td>0.2620</td>
<td>3.8168</td>
</tr>
<tr>
<td>N₂O</td>
<td>π</td>
<td>-0.5099</td>
<td>σ⁺</td>
<td>-0.0544</td>
<td>0.4555</td>
<td>0.2277</td>
<td>4.3917</td>
</tr>
<tr>
<td>N₂O₄</td>
<td>b₁₀</td>
<td>-0.4643</td>
<td>b₁₀</td>
<td>0.4201</td>
<td>0.4441</td>
<td>0.2220</td>
<td>4.5045</td>
</tr>
<tr>
<td>N₂O₃</td>
<td>a''</td>
<td>-0.4302</td>
<td>a''</td>
<td>0.0054</td>
<td>0.4356</td>
<td>0.2178</td>
<td>4.5914</td>
</tr>
</tbody>
</table>

Figure 1. Plot of the energy gap between the HOMO and the LUMO, Δε (a.u.), the global hardness, η (a.u.) and global softness, S (a.u.⁻¹) of the molecular species.

Quantities Δε, η and S of each molecular system are then calculated using the computed energies of their frontier orbitals.

\[ \Delta \varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \]  \hspace{1cm} (1)

where Δε is the difference between the energies of LUMO and HOMO; ε_LUMO is the energy of the lowest unoccupied molecular orbitals, LUMO; and ε_HOMO is the energy of the highest occupied molecular orbitals, HOMO.

\[ \eta = (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) / 2 \]  \hspace{1cm} (2)

where η is the global hardness.

\[ S = 1 / \eta \]  \hspace{1cm} (3)

where S is the global softness.

Δε, η are calculated in hartree unit and S in hartree⁻¹ unit. The computed data of all the molecules are shown in Table 2 and plotted in Figure 1.

From Table 2 we see that the HOMO and LUMO of the nitrosonium cation, (NO)⁺, are σ and π-type respectively and are highly stable. Δε, the height of the gap between the energies of these frontier orbitals, is quite high. This high stability of the frontier orbitals and the large energy gap between them show that the (NO)⁺ system should not be easily susceptible to chemical attack and should be chemically inert. The computed value of global hardness of (NO)⁺ is very high and is close to the hardest of the chemical systems²⁰ and the species is thermodynamically very stable. Although it forms nitrosyl complexes with transition metals and metal analogues, it functions as a very poor σ-donor but strong π-acceptor. A quantum chemical calculation²⁹ has established that (NO)⁺ is a very poor Lewis base and the ratio of the amount of back-donation to donation of charge is 4:1. The poor Lewis basicity and reactivity of (NO)⁺ is also demonstrated by a Localized Molecular Orbital calculation⁰. Thus the computed values of the present theoretical quantities correlate with the high thermodynamic stability and intrinsic chemical inertness of the (NO)⁺ system. Comparing the Δε, η and S of (NO)⁺ with those of other molecules of the series, we see that Δε and η are maximum and S is minimum in the series. Thus, (NO)⁺ is structurally the most stable and chemically the most non-responsive of the series of molecules. Thus the computed theoretical quantities determining the chemical reactivity and stability of the electronic structure of molecules not only reveal the chemical inertness of (NO)⁺ but also justify its position at the bottom of the list of molecules arranged in increasing order of chemical reactivity and at the top of the sequence arranging molecules in the order of stability.

In the case of the N₂O₃ molecule which is extremely unstable and occurs at the top of the list while arranging the molecules in increasing order of reactivity, Δε is small, global softness is high and global hardness is close to the most unstable systems²⁰. The computed values of Δε, η, and S predict that N₂O₃ should be highly chemically sensitive, responsive, structurally unstable and fluxional. The experimental fact is that N₂O₃ is the most chemically reactive and unstable in the series of molecules. When compared with other systems, we find that Δε and η values of N₂O₃ are minimum and S value is maximum in the series. Thus, the present calculation...
not only predicts the extreme instability and chemical reactivity of N₂O₅ but also justifies its position at the top of the series arranged in order of increasing chemical reactivity.

High resonance stability of NO₃⁻ explains the strong acidity of HNO₃ and weak basicity of NO₃⁻. The present computed data show that NO₃⁻ should be structurally stable and unreactive. NO₂⁺ is expected to be harder because of its positive charge than the negatively charged NO₃⁻. But NO₂⁺ is extensively used as a nitrating agent and is more reactive than NO₃⁻. The computed values of Δe and S predict that NO₂⁺ should be more chemically reactive than NO₃⁻. The global hardness of NO₂⁺ is smaller than that of NO₃⁻. This suggests that NO₂⁺, in spite of its positive charge, should be more reactive than NO₃⁻. The well-known reactivity of NO₂⁺ compared to that of NO₃⁻ is theoretically predicted in this calculation.

The computed values of Δe, η and S of the remaining systems, e.g. NO₂⁺, NO₂⁻, N₂O₅, N₂O₄ and N₂O₃ reveal that these molecules should be progressively unstable and chemically reactive. The magnitude of Δe predicts that none of the systems are expected to be highly stable. This is just a corroboration of experimental observations regarding these molecules.

The gradual variation in stability and chemical reactivity in the series of molecules is well represented in Figure 1. The hardness profile and the profile of Δe, the energy gap between the frontier orbitals, increase monotonically starting with the most reactive and structurally unstable species and ending with the most structurally stable and chemically unreactive species. There is a sharp inflexion in the curve around the point of most stable system (NO₃⁻). A close look at the profile of Δe and η reveals that the N₂O₅, N₂O₃, N₂O₄ and N₂O₃ molecules cluster around the same region of the curve. This clustering suggests that the thermodynamic stability and chemical reactivity of these molecules should be very close. The computed data demonstrate that all such systems are unstable and reactive, although there is a small relative variation in the degree of chemical reactivity and stability. The softness profile also reveals the conditions of chemical reactivity and stability of these molecules noted experimentally. The most reactive species is the most soft molecule which occupies the highest position in the softness profile curve. The most stable and unreactive species occur at the lowest position and there is also an inflexion point near their point of occurrence in the curve. The other molecules appear between the most hard and the most soft of the series. The softness profile, like the hardness profile, is thus equally applicable to predict the conditions of chemical reactivity and stability and for a comparative study of such properties of molecules.

The very useful qualitative and quantitative concept of electronic structure and chemical reactivity – the quan-


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