

The nine patterns correspond to different types of participating orbitals: non-bonding, σ -, and π -. In each case, however, the interaction was mediated by two electrons from the donor orbitals. This is just an example. The development of modern chemistry continuously expands bonding concepts to new chemical systems, including systems with a different number of electrons. Considering their increased importance in redox, catalytic, and radical processes, we will discuss a few representative examples of unusual “odd-electron” chemical bonds in the following section.

3.1 Electronic count: two-electron, one-electron and three-electron bonds

Two-electron two-orbital interactions are the most favorable. Once the number of electrons is changed, the benefits of orbital overlap change as well. A simple way to weaken a bond and to diminish the respective stereoelectronic consequences of the direct orbital overlap is to inject either an electron or a hole (i.e. take out an electron, Figure 3.2).

	BDE, kcal/mol	Bond order	Bond type	
$\text{H}_2 \longrightarrow \text{H}^\bullet + \text{H}^\bullet$	101	1	2c,2e	
$\text{H}_2^+ \longrightarrow \text{H}^\bullet + \text{H}^+$	64	1/2	2c,1e	
$\text{H}_2^- \longrightarrow \text{H}^\bullet + \text{H}^-$	52	1/2	2c,3e	

Figure 3.2 Electron counts, bond orders and UMP2=full/6-311++G(d,p) bond dissociation energies (BDEs) for various two-center bonds.

For the symmetric dihydrogen systems, the effects are relatively simple and correlate well with the bond orders – the bond dissociation energy (BDE) in vacuum for a 1e bond in the radical cation is ~60% of the bond dissociation energy for the 2e bond of the neutral H_2 molecule. Interestingly, BDE for the radical-anion is slightly smaller (~50% of that in H_2).

The power of 2c,2e-bonding is further illustrated by He_2^{2+} , a metastable species with a fascinating “volcanic”² combination of kinetic stability and thermodynamic instability (Figure 3.3). The He...He dimer is a weak van der Waals complex with an energy of 8×10^{-6} kJ/mol and a He-He “bond” length of ca. 6.2 Å. In contrast, the corresponding dication He_2^{2+} has a large (33.2 kcal/mol) barrier to dissociation despite the 200 kcal/mol exothermicity originating from the strong Coulombic repulsion of the two positive charges.³ Interestingly, the very short He-He distance of 0.704 Å is shorter than both the H-H bond of the hydrogen molecule and “the world’s shortest bond” of the H-T molecule, the heavier isotope of H_2 .⁴

The oxidative approach to the formation of chemical bonds by removal of electrons can be extended to relatively complex organic molecules in solution. For example, neutral 1,6-diazabicyclo[4.4.4]-tetradecane (with the N-N distance of 2.806 Å) is transformed upon removal of two electrons into a N^+-N^+ dication,

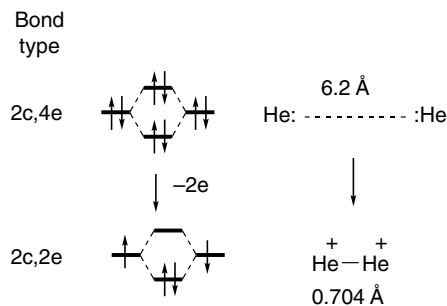


Figure 3.3 Making bonds by removing electrons: contrasting He...He distances as function of number of electrons.

where the distance between the positively charged nitrogen atoms is reduced to 1.532 Å (Figure 3.4).^{4,5} Formation of the N-N bond is particularly noteworthy – not only does it overcome Coulombic repulsion and bring the formally positively charged nitrogen atoms closer than their uncharged forerunners but it corresponds to the strained “intra bridgehead” bond type. A similar transition from the non-bonding interactions between two lone pairs into a 2c,2e bond between two cationic S-centers is observed in 1,5-dithiacyclooctanes.⁴

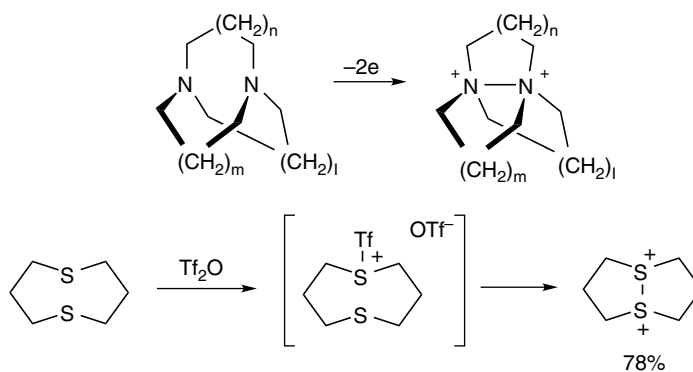


Figure 3.4 Formation of chemical bonds by removal of electrons.

In a similar way, 2c,2e π -bonds can also be formed by removal of electrons. For example, the O-O distance in the O_2^{2+} dication, 1.073 Å, is 0.134 Å shorter than the bond in molecular oxygen. This distance, considered to be the shortest bond between any two heavy atoms, is even shorter than the N-N distance in the isoelectronic N_2 molecule (1.098 Å).

The consequences of changes in electron count for the stabilizing effect of π -overlap can be explored further via comparison of rotation barriers in alkenes with their one-electron reduced and oxidized counterparts. In ethylene, the barrier for the 90° twist approaches 65 kcal/mol (Figure 3.5).⁶ This relatively high value is still most likely an underestimation of the π -bond energy because the energy cost is partially compensated by strong stabilization of the radical centers in the twisted structure by hyperconjugation.⁷

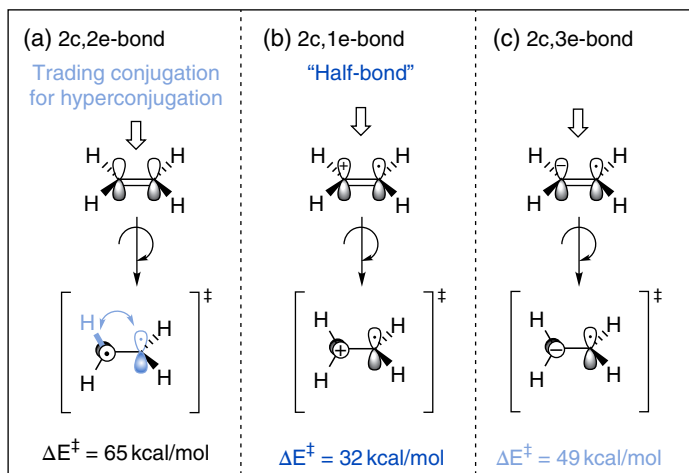


Figure 3.5 Energy costs for the 90 degree twist in (a) ethylene (experimental), (b) ethylene radical cation (MP2/6–31G**), and (c) ethylene radical anion (B3LYP/6–311++G(3df,3pd)).⁸

On the other hand, conversion of ethylene into the radical cation changes the 2c,2e π -bond into a 2-center, 1-electron (2c,1e) “half-bond.” As a result, the energy cost for the rotation is decreased to $\sim 32 \text{ kcal/mol}$, approximately half of the original value in the neutral system. The 2-center, 3-electron (2c,3e) bond in the radical anion is also weakened in comparison to the “normal” 2c,2e bond, as the extra electron now populates an antibonding MO. The barrier for rotation in ethylene radical-anion is significantly lowered relative to that in the parent ethylene (from 65 to 49 kcal/mol, Figure 3.5).⁸ This example illustrates that the importance of stereoelectronic constraints may change dramatically in odd-electron “half-reduced” or “half-oxidized” species. The differences in the rotation barriers between the 1e- and 3e-systems are likely to originate from rehybridization and hyperconjugation effects in the twisted species.

The relatively high stabilization provided by 2c,3e-bonds can explain why the triplet state of molecular oxygen is a favorable electronic alternative to the singlet O_2 . Students are often confused by the seeming contradiction between the following two experimental data: a) the *paramagnetic* properties of O_2 suggest the presence of unpaired electrons, but b) the O–O bond length in O_2 (1.21 Å) is close to the expected value for a double bond (a typical O–O single bond is ca. 1.48 Å). However, these “contradicting” observations are reconciled once the double bond of O_2 is made from a σ -bond and two three-electron π half-bonds (Figure 3.6). This description reconciles the overall bond order of two *and* with the presence of two radical centers.

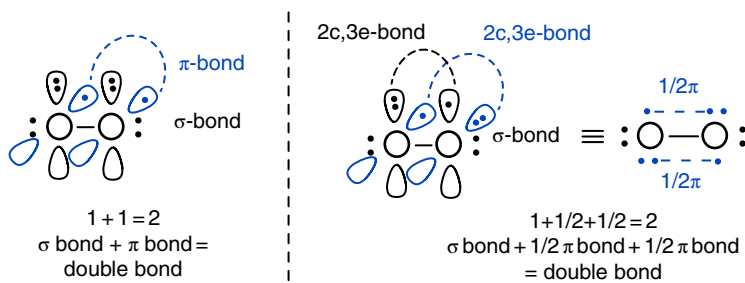


Figure 3.6 Two ways for making a “double” bond.

Three-electron bonds are far from being just chemical curiosities – they are encountered in many persistent radicals (e.g. 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (=TEMPO), nitric oxide (NO), ketyl). Their formation (sometimes transient) can lead to significant consequences for reactivity. For example, strong 2c,3e bonds provide additional stabilization to the conjugate base of α -hydroxy radicals, explaining the much higher OH acidity in these compounds in comparison to the acidity of normal alcohols (Figure 3.7).⁹

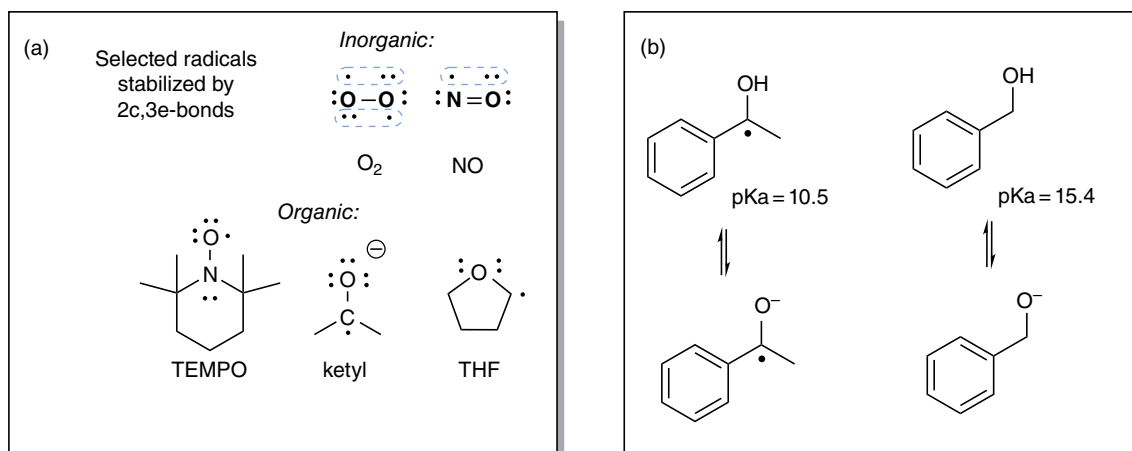


Figure 3.7 (a) Selected examples of radicals stabilized by 2c, 3e bonds. (b) 3e bonding can be used to stabilize anions as well.

Stabilization provided by 2c-3e bonds has also been used in the design of radical fragmentations. Although the C-C bond is generally hard to break, the introduction of an O or an N atom next to the incipient radical center facilitates the C-C bond cleavage greatly (Figure 3.8).¹⁰

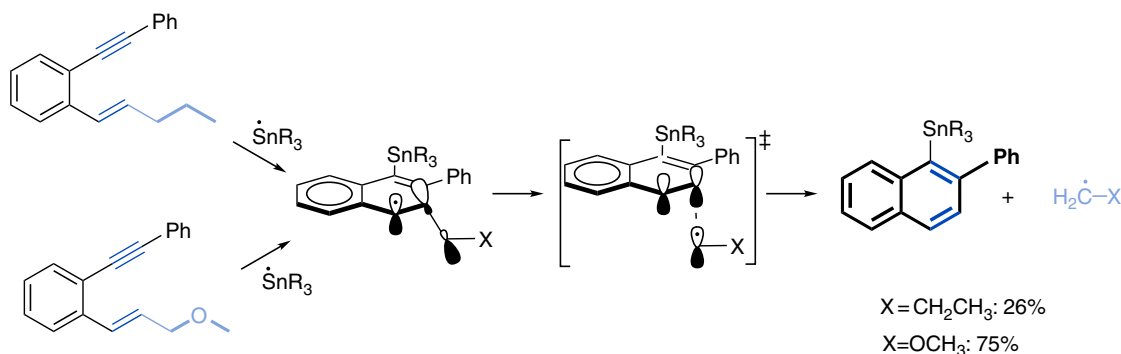


Figure 3.8 Formation of 2c-3e bonds can be used to facilitate C-C bond cleavage.

Of course, no π -bond can be formed *without* electrons in the π -orbitals and, as expected, the planar conformation of ethylene dication has a relatively long 1.587 Å bond. In a sharp contrast to the neutral ethylene, the ethylene dication is stabilized by 28 kcal/mol in the “perpendicular” geometry, formed upon 90° rotation around the C-C bond. In the more stable twisted geometry, the C-C bond is relatively short (1.398 Å,

MP2/6-31G*), due to the strong $\sigma_{\text{C-H}} \rightarrow \text{p}^+$ hyperconjugative interaction of the two cationic centers with vicinal C-H bonds.¹¹ For the same reasons, the planar conformation of $\text{BH}_2\text{-CH}_2^+$ is ~ 25 kcal/mol less stable than the perpendicular conformation (Figure 3.9).¹²

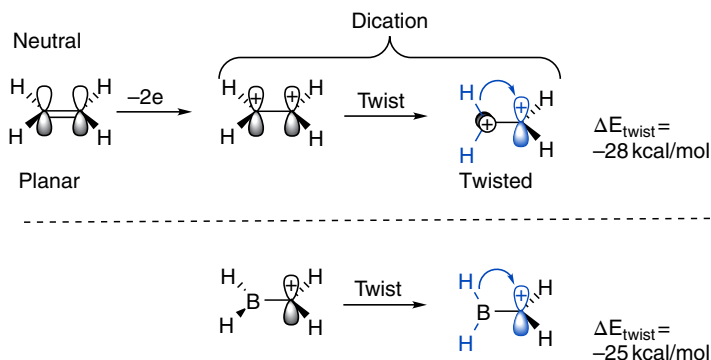


Figure 3.9 “Zero-electron bonds” provide no stabilization, as illustrated by the twisted geometry preference for systems without π -electrons at the two adjacent sp^2 -hybridized atoms.

The number of electrons changes stability in a more complex way in three-center systems, i.e. the allyl and related species. In this case, delocalization of charge is much more important than delocalization of spin. For example, rotation around the C-C bond becomes much more difficult in the allyl cation (~ 38 kcal/mol) compared to the allyl radical (~ 13 (calculated), 15.7 (experimental) kcal/mol).¹³ Allylic anions have a lower rotation barrier relative to the cation (~ 23 vs. ~ 38 kcal/mol).^{14a} In the case of anions, additional stabilization to the twisted form (~ 8 – 14 kcal/mol) is provided by rehybridization, which partially offsets the lower efficiency of hyperconjugation in the twisted anion than in the twisted cation. The calculated barriers for the allyl system depend strongly on the methods employed, but the trend of cation > anion > radical remains. The same trend is observed for the rotation barriers in the benzyl radical and cation (Figure 3.10).¹⁵

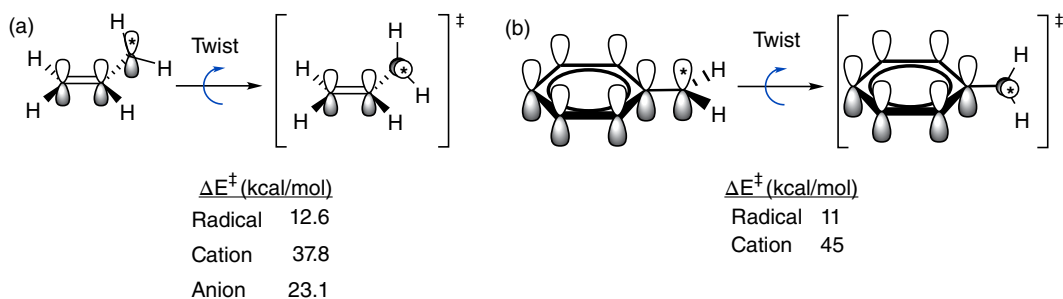


Figure 3.10 Energy costs for the 90° rotation in the (a) allyl radical, cation, and anion; (b) the benzyl radical and cation.

The rotational barrier in allyl radicals also illustrates the effect of the number of orbitals in the conjugated array on the conjugation. Removing one p-orbital from conjugation via the 90° twist in allyl radical imposes the energy penalty of only ~ 15 kcal/mol – considerably less costly than the penalty for the analogous rotation in ethylene (~ 65 kcal/mol).