Molecule Matters

Dinitrogen

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Dinitrogen (N_2) is a very stable and inert molecule due to the formation of a triple bond between the two atoms. Surprisingly isoelectronic molecules are quite reactive making dinitrogen very useful and unique.

Dinitrogen (N_2) is such an innocuous molecule that you might not think it worthy of special attention. We take this molecule for granted because it is abundantly available on earth. About 80 % of the earth's atmosphere, which means a total of 4×10^{18} kg, is dinitrogen![1] Secondly, it is ignored because it is quite unreactive. Nitrogen is such a stable molecule that it will not react with most elements [2]. As the most inert molecule of all the first row diatomics, one can hardly feel its presence even though it is present in such abundance. The presence of such an inert material in air is responsible for slowing down the process of burning. If it were not for nitrogen, many things would burn (react with oxygen) with explosive violence! It is this very property of nitrogen that makes it very special.

Measuring Inertness

The chemical inertness of dinitrogen almost equaling that of inert gases is quite surprising. Inertness can be related to the reluctance to share, donate or take up electrons. This in turn can be related to two fundamental properties: the ionization potential (IP) which is the energy required to remove one electron completely, and electron affinity (EA), the energy liberated on addition of an electron. By convention, EA is the negative of the experimentally measured value. When two molecules form a weak complex, the interaction might just distort the electron cloud around the molecules instead of sharing electrons or transferring an electron

Molecules	Ionization Potential (eV)	Electron Affinity (eV)
H_2	15.43	−2.0
B_2	–	>1.30
C_2	11.41	3.54
N_2	15.58	−1.6
O_2	12.07	0.43
F_2	15.69	2.9
CO	14.01	−1.33

Table 1. Ionization potential and electron affinity of diatomics.

from one to the other. The reluctance of the electron cloud to undergo distortion is called the hardness and is the opposite of polarizability. Hardness must be related to both quantities IP and EA. Recently it has been argued that the average of the two values is the absolute electronegativity and the difference between IP and EA the absolute hardness [3]. The latter gives us a measure of the energy required to distort the electron cloud. With this background, take a look at some of these fundamental quantities for the diatomics formed by the first row elements [4,5]. (See *Table* 1.)

The combination of negative electron affinities and high ionization make, H_2, N_2 and CO special. The reason for this can be traced to the very strong bonds formed in these molecules by sharing electrons. So let us take a careful look at the bonding in N_2.

Bonding Model

The molecular orbital energy level diagram for homonuclear diatomics formed by Li to N is available in most textbooks. One fact that often confuses students is the unusual ordering of the σ and π orbitals. The HOMO (highest occupied molecular orbital) of N_2 is a pair of non-bonding orbitals on N and not the degenerate set of π orbitals. This 'strange' ordering of molecular orbital energies is due to a subtle interaction or mixing of the '2σ' and '3σ' molecular orbitals formed from mixing $2s$ and $2p_z$ orbitals of
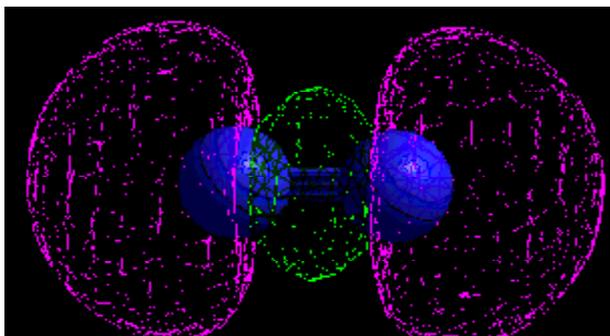
each atom. As one proceeds from left to right in the periodic table, the energy difference between 2s and 2p keeps increasing. As a result, there is less mixing in dinitrogen. The 3σ in dinitrogen is just above the π leading to an orbital energy level diagram shown in textbooks. A pictorial rendering of the 3σ and 1π wave functions is given in *Figures* 1 and 2 respectively.

Bond Energy

Both valence bond and molecular orbital theories correctly predict the presence of a triple bond between the two nitrogen atoms which is the maximum bond order observed for the first row elements. So it is not surprising that N$_2$ has the largest bond dissociation energy (BDE) for any homonuclear diatomic in the whole periodic table [6]. Interestingly, if only single bond energies are considered, the average N-N single bond is significantly weaker than the average C-C single bond (*Table* 2). But the homonuclear diatomic molecule C$_2$ is more easily dissociated than N$_2$ because of the bond order which turns out to be two for C$_2$ but three for N$_2$. One answer that is offered for the weakening of the N-N single bond is the presence of the lone pair of electrons on the two nitrogens. They repel each other leading to a smaller BDE. In support of this hypothesis, O and F have weaker single bond energies as they have two and three lone pairs respectively.
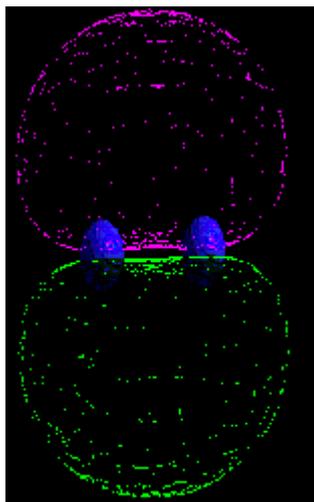
Reactivity

The inertness of dinitrogen gives a misleading impression that it may be completely unreactive. That is not true. Reactive metals
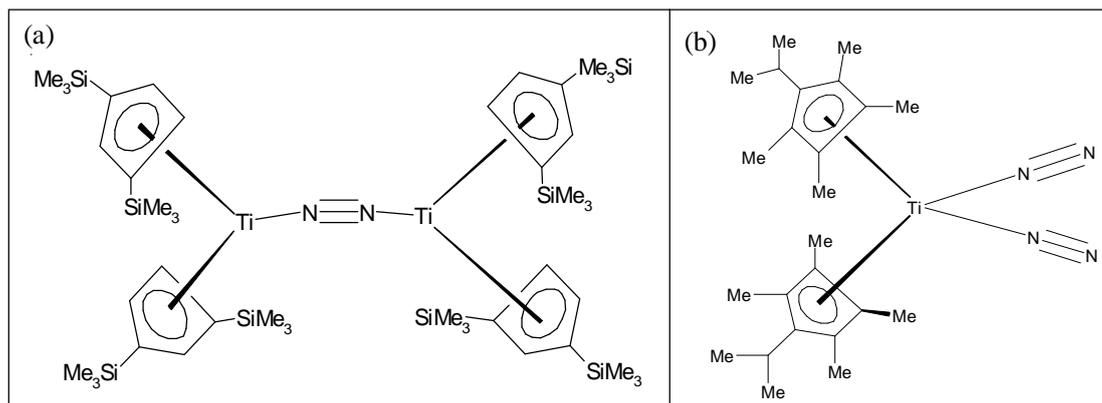
	H	C	N	O	F
H	432				
C	411	346 602(2) 835(3)			
N	386	304 615(2) 887(3)	167 418(2) 942(3)		
O	459	358 799(2) 1072 (3)	207 607(3)	142 494(2)	
F	565	485	283	190	155

Table 2. Mean Bond Enthalpies* in kJ mol⁻¹ [6]. * Values are for single bonds except where the bond order is given in parentheses.

like lithium, magnesium and titanium react directly with nitrogen under the right conditions. They can 'burn' in an atmosphere of nitrogen to give nitrides. Interestingly, there are several compounds where dinitrogen donates a lone pair of electrons to other transition metal ions [7]. (See *Figure* 3.) These compounds show N_2 coordinating in an end-on position. However compounds where N_2 is symmetrically coordinated as in *Figure* 3a, to two metals, are nearly ten times more common! Based on the ionization potentials, the donation of the π electrons on dinitrogen is just as easy as donation of the lone pair. There are fewer complexes of dinitrogen where the N_2 molecule is found coordinated in a side-on fashion (*Figure* 4).

Figure 3 (a) End-on coordination of N_2 (bridging mode). (b) End-on coordination of N_2 (terminal mode).
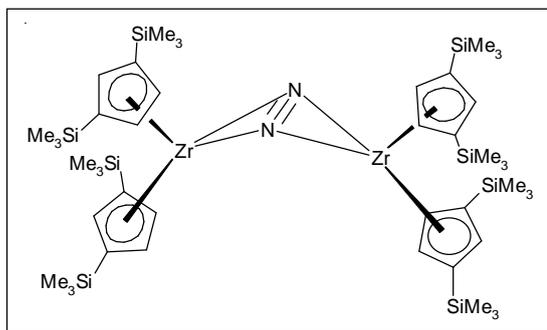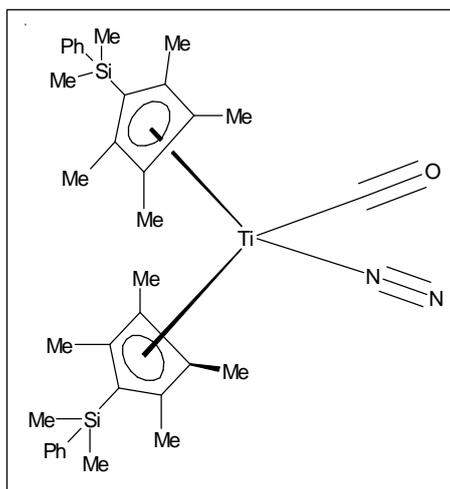
Figure 4 *Side-on coordination of N_2.*

The meager coordination chemistry of dinitrogen *vis-à-vis* the extensive coordination chemistry of isoelectronic CO is puzzling at first sight. CO is unique because it binds to many low oxidation state metal complexes. The metal is electron rich and gives electron density back to the CO. This back bonding stabilizes the M-CO bond and is synergistic in nature. The contribution of C to the π* in CO is significantly higher than the contribution of O. This leads to good M-C overlap and stabilization. So the π* orbital on CO is specially suited for back donation from the metal. In dinitrogen, both atoms of N have equal contribution resulting in smaller overlap and weak π acid character. In the light of these unfavorable factors, it is surprising that Chirik and co-workers managed to characterize a N_2 complex with Ti in the presence of CO. This molecule is shown in *Figure* 5 [7].

The Role of Nitrogen in Life

The element nitrogen plays a very important role in molecules of life: proteins and nucleic acids. It is nitrogen that gives many organic compounds their basic nature. But most plants and animals cannot use dinitrogen directly to make these vital molecules. The special enzyme nitrogenase, is required to convert dinitrogen to useful compounds that can be assimilated by plants. This enzyme is present only in a few bacteria. It is remarkable in that it converts nitrogen from its zero oxidation state in dinitrogen to derivatives of ammonia where N is in its (–3) oxidation state. The reduction requires the formal addition of 6 electrons to dinitrogen and this has to be done in the absence of oxygen. The enzyme carries out this difficult conversion under ambient conditions with the help of two transition metal ions Fe and Mo. In some forms of the enzyme, Mo is not found. But all variations of nitrogenase have a cluster of Fe and S atoms. No other element can be substituted for iron! 'Inorganic' iron

Figure 5. *A titanocene complex with both N_2 and CO.*

turns out to be the essence of life. A detailed description of nitrogenase is beyond the scope of the present article but is an area of active interest [8].

In order to appreciate the nitrogenase enzyme we need to look at the thermodynamics of this reaction and also the best artificial catalyst and reaction conditions available to date for this process.

$$N_2 + 3H_2 \leftrightarrows 2NH_3$$
$$\Delta H = -92.4 \text{kJ mol}^{-1}, \quad \Delta G^0 = -39.2 \text{ kJ mol}^{-1} \text{ at 273 K.}$$
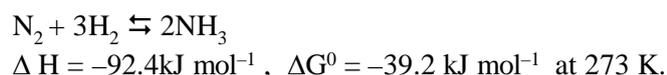
Fritz Haber who discovered the process for converting dinitrogen to ammonia was awarded the Nobel Prize in 1918 for this contribution. He used a total pressure of 200 atm and temperatures ranging from 400–500°C for the synthesis of ammonia in the presence of osmium catalysts and uranium carbide [9]. Until then, several researchers had attempted the direct combination of elements to synthesize ammonia and failed. The reaction has had far-reaching consequences for agriculture where ready access to ammonia is very important for the synthesis of fertilizers. The application of fertilizers increases the yield of plants nearly 5-fold. Without fertilizers, there would have been no green revolution. Haber conceded in his Nobel Lecture [10] that "Nitrogen bacteria teach us that Nature, with her sophisticated forms of the chemistry of living matter, still understands and utilizes methods which we do not as yet know how to imitate."

Isoelectronic Molecules: CO, CN⁻, NO⁺

While dinitrogen is special because it is so inert, the isoelectronic molecules have interesting reactivity patterns! Consider CO, its most infamous analog. This heteronuclear diatomic is very similar to dinitrogen. It is reasonably inert and has very large bond dissociation energy. However, it is a terrible poison as it cannot be smelt and can kill humans when they are exposed to 800 ppm for greater than one hour. It binds to haemoglobin irreversibly making it useless for transporting oxygen. Interestingly, a recent report claims that trace amounts of CO have been detected in the body and declared to be an 'essential molecule' for protecting the

Suggested Reading

[1] Gary W Vanloon and Stephen J Duffy, *Environmental chemistry*, Oxford University Press, 2000.

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[4] John P Lowe, *J. Am. Chem. Soc.* Vol.99,No.17, pp.5557–5570, 1977.

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[6] J E Huheey, E A Keiter, R L Keiter, *Inorganic chemistry*, Pearson education Asia, 2002.

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[9] F Haber, *Zeitschrift fur Angewandte Chemie*, Vol. 42, No.23, pp.647-648, 1929.

[10] http://nobelprize.org/ nobel prizes/chemistry/ laureates/1918/haber-lecture.html, Nobel lecture of Haber, pp.326–340, 1920.

[11] http://en.wikipedia.org/ w/index.php?title= Nitrogen&oldid=81787292. Nitrogen. *In Wikipedia, The Free Encylopedia.*

[12] Jayant M Modak, Haber Process for Ammonia Synthesis, *Resonance*, Vol.7, No 9, pp.69–77, 2002.

heart. The cyanide ion is very similar to CO in that it binds to haemoglobin rendering it useless. The sodium or potassium salts are the deadliest forms as they dissociate readily. About 2.8 mg/Kg of body weight is lethal. The biological effect of NO^+ is not commonly known but it is likely to be reduced to NO which is a very important signalling molecule in the cell. What makes the iso-electronic molecules N_2, CO, CN^-, NO^+ to behave so differently?

Inertness Makes it Useful

Apart from these interesting 'academic' facts about dinitrogen, one should not forget that there are several uses for it. The most common use for dinitrogen is its utility in preservation of food and its use as a cryogenic fluid. The liquid boils at 77 K and freezes at 63 K. As a result, liquid N_2 is used to preserve many food and biological materials in a frozen condition. It is used extensively in laboratories as a cryogen. Cooked food can be oxidized or become rancid in contact with air. If the packing is done under inert atmosphere, the food inside the package is safe from oxidation and the 'freshness' is preserved. Potato chips, coffee, and several fully cooked meals are packed under nitrogen to preserve freshness. Since nitrogen is readily available in the atmosphere, it is convenient to use this molecule as an inert blanket while welding where the joint has to be protected from oxidation especially when it is hot. More uses for this 'noble' molecule are available in the textbooks and in the open source encyclopedia [11].

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