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BOND CHARACTER AND THE METASTABILITY OF PLOSOPHORIC GROUPS OF MILITARY SIGNIFICANCE

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INTRODUCTION: The usual calculation of chemical bond energy from electronic orbitals is difficult and subject to great variation in accuracy. Appendix A describes a simple algorithm for calculating bond energy. The algorithm utilizes the experimental interatomic distances, the assumed electronic orbitals, and the change in energy for an atom determined by the amount of charge localization. Variables may be introduced into the electronic orbitals and charge distributions varied to obtain minimum energy conditions. Similar calculations give the bond energies for molecular ions. Then the ionization potentials of molecules may be determined. Table I compares calculated and experimental values of bond energies and ionization potentials for several diatomic molecules.

TABLE I

Comparison of Calculated and Experimental Bond Energies and Ionization Potentials for Some Diatomic Molecules

Molecule	Bond Energy		Ionization Potential	
	Calculated	Experimental	Calculated	Experimental
H_2	4.809	4.476	15.64	15.6
N_2	9.845	9.756	15.34	15.51
NO	6.482	6.487	9.69	9.5
O_2	4.952	5.08	-	-

For the original calculations, the atomic electronic energy was determined using Slater's [1] rules. However, difficulty was encountered when heavy atoms were incorporated into hetero-nuclear molecules. Investigations revealed that although Slater's rules may be used to approximate the total energy of the atoms, they do not accurately give the first ionization potential for many atoms.

This problem has been resolved by retaining the form of the energy terms used by Slater, but determining the constants from experimental atomic ionization potentials of the valence electrons.

Although the procedure for calculating the molecular bond energy is of interest, in this paper primary emphasis will be given to the results obtained for the group of compounds known as the azides. Sodium azide (NaN_3) and potassium azide (KN_3) are relatively stable compounds. Lead azide ($Pb(N_3)_2$), used extensively as a primary explosive, hydrazoic acid (HN_3), and silver azide (AgN_3) are representatives of the less stable azides.

The bonding molecular orbitals in the azide group and the electronic charge distribution on the atoms cha··· depending on the nature of the bond to the cation and the ionization state of the azides.. Usually this distinction is made on the basis of ionic or covalent bonding to the cation. Evans and Yoffe[2] pointed out the influence of the ionization potential of the metal, or cation, on the nature of the bond to the azide. The results of the present work indicate that in addition to the effect of ionization potential, a covalent bond has characteristics that extend beyond the nearest neighbor atoms. This extension of the covalent bond over several atoms is a result of the delocalization of the electronic orbitals over the entire molecule.

The discussion that follows will cover first N_3^-, its ionization to form N_3, and further ionization to form N_3^+. Next, the effect of atomic ionization potentials and the requirements necessary to form ionic or covalent bonds will be investigated. Then it will be possible to compare different mechanisms of decomposition.

The Azide Ion, N_3^-. The sixteen electrons in the valence shell for N_3^- must be assigned to electronic orbitals. From the experience that has been gained in working with this method of calculating bond energies, it has been found that arbitrary assignment of the density of electrons in some orbitals may be offset by providing variability in other orbitals. The assignment for the electronic density on each atom for different molecular orbitals is given in Table II.

TABLE II
Distribution of Electrons for Calculating the Bond Energy for N_3^-

Type of Orbital	Electron Density		No. of Electrons
	End Atoms	Center Atom	
σ_g^-	0	1	2
σ_u	c_1	$1-2c_1$	2
π_u	c_2	$1-2c_2$	4
π_g	1/2	0	4
σ_g^-	1/2	0	2
σ_u	1/2	0	2

The bond energy calculated for N_3^-, using an assumed N-N distance of 1.16Å, is 299.8 kcal/mole. This value is in excellent agreement with the enthalpy of formation for N_3^- given by Gray[3] of 34.8 kcal/mole. Converting the enthalpy of formation to bond energy for the N_3^-, one obtains 302.7 kcal/mole.

The electronic charge distribution on the N_3^- is also obtained from the minimization of the energy. It is found that the central nitrogen atom has a charge of +0.92|e|. Bonnemay and Daudel[4] give +0.66|e| for the value of this charge.

The Azide Radical, N_3. The removal of a single electron from N_3^- will produce N_3. Since the πg orbital is non-bonding, this is a likely orbital for losing the electron. The calculation of the bond energy for this configuration, using the same interatomic distances as for N_3^-, yields 235.8 kcal/mole, or an electron affinity for N_3 of 64 kcal/mole. This value for the electron affinity agrees with Gray's[3] value of 69 ± 7 kcal/mole.

The Positive Azide Ion, N_3^+. As in proceeding from N_3^- to N_3 it was expected that an electron would be removed from the π g orbital, so in going from N_3 to N_3^+ the single electron should be removed from the πg orbital. When the interatomic distance of 1.16Å is used also for N_3^+, the calculated ionization potential is 266.5 kcal/mole compared to Gray's value of 283 ± 6 kcal/mole. Although the calculation appears to be low, it is in excellent agreement with some experimental results of Franklin, Dibler, Reese, and Krauss[5].

Nature of the Cation-Azide Bond. When will a metal azide be ionic? Some attempts have been made to answer this question by considering the ionization potential of the metal as the determining factor. In the following discussion the relationship between the metallic ionization potential and ionic character will be derived.

Consider an azide ion and a metallic positive ion. Assume no polarization of the azide ion then a minimum energy (maximum bonding) will be achieved for a linear configuration.

$$
\begin{array}{cccc}
M & N & N & N \\
+1. & -.86 & +.96 & -.86
\end{array}
$$

For this configuration the energy will be given by

$$E_{Ionic} = I_p - E_A + E_c$$

where I_p = ionization potential of the metal

E_A = electron affinity of the azide radical, and

E_c = coulombic energy of the system.

If the azide is to be ionic, this energy must be less than the energy that can be obtained from covalent bonding. The pure covalent bond energy may be approximated by the method of Appendix A to be:

$$E_{covalent} = \frac{3.598}{r}$$

where r is the metal-nitrogen bond distance in angstroms and the energy is given in electron volts (ev). Thus, an azide is ionic when

$$I_p < I_{Max}$$

when $I_{Max} = E_A - E_c + E_{Covalent}.$ (I)

Since both E_c and $E_{Covalent}$ are functions of r, the maximum ionization potential, I_{Max}, that a metal may have and still form an ionic bond is determined by the metal-nitrogen bond distance. Some values for I_{Max} as a function of r are given in Table III.

TABLE III

Maximum Ionization Potential for Ionic Azides
as a Function of the Metal-Nitrogen Distance

r. (Å)	I_{Max} (e.v.)
1	11.2
1.5	8.45
2.0	7.12
2.5	6.34
3.0	5.82

Although pure ionic or pure covalent bonding seldom exists, the mixing of the two types of bonding will be most noticeable when the cation ionization potential is approximately equal to I_{Max}.

To use Equation I, let us assume a radius of 0.58Å for the end nitrogen atom of the azide ion, use the ionic radius for the cation, and compare the calculated maximum ionization potential with experimental ionization potential for the metal. The results of these calculations are given in Table IV for several metals which form monovalent azides.

TABLE IV

Comparison of I_{Max} and Experimental Ionization Potentials

Metal	Assumed r (Å)	Equation I I_{Max} (ev)	Experimental I_p (ev)	Difference $I_{Max}-I_p$
Ag	1.84	7.50	7.542	-0.042
Tl	2.05	7.05	6.07	0.98
Cu	1.54	8.30	7.68	0.62
Na	1.55	8.26	5.12	3.14
K	1.91	7.33	4.318	3.012
C_s	2.25	6.70	3.87	2.83

These results may be divided into two categories. The first group consists of those metals with the difference, $I_{Max}-I_p$, less than one electron volt. In this group we have Ag, Tl, and Cu.

The second group contains the alkali metals with a difference of approximately three electron volts. The alkali metals bonds are ionic, but the metals of the first group may form bonds that are ionic, mixed, or covalent depending on actual bond length. The mixed bonding mechanism is the most probable.

A similar derivation may be made for the divalent metals using their first two ionization potentials. The maximum sum of these two ionization potentials will be given by:

$$I_{Max} = 2E_A - E_c + 2E_{Covalent}$$

A factor, two, occurs since there are two azide ions and two covalent bonds. The coulombic energy must be calculated for a given configuration. Calculations based on a linear molecule and the doubly ionized atomic radii yield the following results.

Metal	Calculated	Experimental Sum	Difference
	I_{Max} (ev)	$I_{p1} + I_{p2}$	I_{Max} - Sum
Ba	20.7	15.14	5.56
Sr	22.6	16.55	6.05
Ca	24.4	17.91	6.49
Mg	29.1	21.57	7.53
Pb	21.9	22.34	- .44
Cd	24.6	25.8	-1.2
Hg	23.1	29.08	-5.98

If the ionization potential were considered as the only criterion for the nature of the bond, Mg and Pb would be expected to have much the same bond characteristics. However, the results in the last column indicate that the bonding should be different.

The above calculations were made on the basis of the radii of doubly ionized atoms. For PbN_6 and SrN_6 the metal nitrogen bond length was taken to be 1.78Å and 1.7Å, respectively. For each of these azides the bond length in crystals is approximately 2.6Å [6-8]. This new length corresponds to a value of 16.6 ev for I_{Max}. For PbN_6 this means that the molecule becomes more covalent. For SrN_6 the trend is toward a more covalent bond also, but since SrN_6 was originally considered to be an ionic bond, the actual bond has a mixed ionic and covalent character.

Bond Energy of HN_3: The molecular orbitals used in the calculation of the energy of N_3 leave an unpaired electron in a Π g orbital on the end nitrogen atoms. This orbital may be mixed with the 1s orbital of the hydrogen. The coefficients of the molecular orbitals may be varied to give a maximum bond energy which is 290.7 kcal/mole, when the experimental values are used for bond lengths.

Another mode of bonding the hydrogen to the azide is to assume a localized covalent bond to one of the end nitrogen atoms. For the experimental bond lengths this yields a value 18.1 kcal/mole more stable than the delocalized model. Since the localized bonding is more stable, it will be taken as the electronic configuration for HN_3. Then the estimates of the individual bond energies in kcal/mole are:

$H - N_3$	82.3
$HN - N_2$	73.9
$HN_2 - N$	152.6

It should be pointed out that these bond energies are not necessarily the energy required to separate the molecule into two parts at the given bond. These energies are the calculated values for the given bond. In those cases where electrons are shared between two non-adjacent atoms, the energy is assigned to adjacent atom bonds.

The total bond energy of 308.8 kcal/mole is to be compared to the value given by Gray[3] of 318 kcal/mole. The calculations are based on the formation of a gas molecule, but at $25°C$ HN_3 is a liquid. If it is assumed that Trouton's rule[9] may be used for HN_3, then the heat of vaporization at the melting point, $37°C$, is 6.8 kcal/mole. Gunther, et al,[10] measured the heat of vaporization at $12.4°C$ to be 7.3 kcal/mole. This correction brings the calculated value to within one percent of Gray's value.

Bond Energy of PbN_6: The bond energy calculations for lead azide do not permit a clear choice between the localized and the de-localized models for the covalent bond. The ambiguity in bonding is not present in the calculation for HN_3. Two characteristics of PbN_6 which differ from HN_3 may account for this ambiguity. The first difference is a longer bond between the metal and the azide. The second difference is the coulombic repulsion of charges on the two azide groups of PbN_6.

Consider the longer bond length between the metal and the azide. For the calculations of bond energy this length for PbN_6 was taken as $2.6Å$. This value is slightly longer than the shortest value for the bond length of $2.48Å$ measured by Glen.[6] However, it is considerably shorter than his longest value of $2.97Å$. When a local-ized bond is changed to a delocalized bond, the decrease in bond strength of the metal-azide bond is proportional to the original localized bond strength. Since the delocalization of the electrons strengthens the azide bonds independent of the metal-azide bond length, total bonding of the molecule by delocalization may increase even though the metal-azide bonds are weaker. The long bond of PbN_6 favors the delocalization of the bonding electrons over the entire azide group.

Coulombic repulsion between the two azide groups must be considered for both the localized and the delocalized models of

PbN_6. Such coulombic repulsion does not have to be considered for HN_3 since there is only one azide group per molecule. In the delocalized model the repulsion between groups is offset by coulombic attraction within the azide groups. The localized model does not have this additional coulombic attraction within the azide groups. Thus the total strength of the bonds within the azide will be stronger for the delocalized model.

The energy calculations for both models of PbN_6 yield 538 kcal/mole which is equivalent to a heat of formation of 137 kcal/mole. Since the calculations are based on the formation of a gas molecule, it is not surprising that the experimental heat of formation for crystalline PbN_6, 115 kcal/mole,[3] is less than the calculated value. This difference of 22 kcal/mole represents the additional bonding that results from crystallization.

Although both models yield the same total bond energy, the distribution of energy between the bonds is different as shown in Table V.

TABLE V
Bond Energies of PbN_6 (kcal/mole)

Bond	Localized Model	Delocalized Model
$Pb - N_3$	42.4	26.6
$PbN - N_2$	73.9	121.2
$PbN_2 - N$	152.6	121.2

In the calculation of bond energy for PbN_6, the 1/2 hv terms have been assumed to be the same as the similar terms in N_3^-. This accounts for 8 of the 15 vibrations. Since the $Pb-N_3$ bond is weak, these vibrations should be of low energy and weaken the bond only slightly. However, it should be remembered that if hv $<$ kT then each vibration will have an energy, RT, which will weaken the bonding. At $300°K$ this weakens each $Pb-N_3$ bond by 2.1 kcal/mole.

Choi and Boutin[8] have studied the crystal structure of alpha lead azide. They found that the azide groups are linear. Some of the groups are symmetric while others are asymmetric. This agrees with the fact that both models for PbN_6 give the same bonding energy. In each case the azide is linear, but only for the delocalized model of bonding will the azide group be symmetric.

The amount ionic bonding in PbN_6 is indicated by the amount charge moved from the lead to the azides. For the localized model this is 0.53 electrons and for the delocalized model it is 0.64 electrons. Since 2 electrons must move to be fully ionic, it is clear that PbN_6 has mixed ionic and covalent bonding.

Decomposition Kinetics: The covalent bonding of HN_3 and PbN_6 discussed in the preceeding sections make it possible to propose

mechanisms for the decomposition of these azides. It is clear that the weakest bond for HN_3 is the weaker of the two bonds in the azide group whereas for PbN_6 the bonding of the azide to the lead is the weakest bond. The decomposition of these azides should proceed by the rupture of these weak bonds.

For HN_3 in the liquid state the reaction $HN_3 \rightarrow HN + N_2$ is endothermic by 9 kcal/mole and for the gas phase it is endothermic by 2 kcal/mole. These energies represent the difference between the energies of the ground states of the molecules. It should not be concluded that this is the activation energy for the reaction. Although the reaction in the gas phase is a forbidden combination, in a liquid the forbidden condition may be relaxed. The activation energy for the unimolecular reaction is that energy necessary to break the bond plus the endothermicity or 83 kcal/mole.

A bimolecular reaction will proceed with a lower activation energy. An estimate[11] of this energy is 39 kcal/mole for the gas phase and 46 kcal/mole for the liquid. Gray and Waddington[12] studied the spontaneous detonation of HN_3 as a function of temperature and pressure. An analysis[13] of this data yielded an activation energy of 37 kcal/mole for an assumed bimolecular reaction process.

For PbN_6 the reaction will occur on a surface. Since this is not a gas phase reaction, the energy of sublimation must be included in any energy calculations. The weak bond occurs between the lead and the azide. Although this is the bond which first breaks in a bimolecular reaction, at least two azide radicals will continue to react forming three nitrogen molecules and releasing sufficient energy to make the total reaction exothermic. The estimated activation energy for a bimolecular reaction is 15 kcal/mole when the delocalized bonding model is assumed, and 23 kcal/mole when the localized bonding model is assumed. Baum[14] found an activation energy of 26 kcal/mole for thermal decomposition of PbN_6. Although this energy seems to be in agreement with the localized bonding model, a recent theory[15] discussing the initiation of PbN_6 shows that an activation energy of about 18 kcal/mole can yield under certain conditions an apparent activation energy of 26 kcal/mole.

Summary: The algorithm, described in the appendix, for calculating bond energies has been used successfully to calculate bond energies for the azides. Not only can the total bonding of the molecule be calculated, but the individual bonds within the molecule may be estimated. These individual bond energies provide a basis for estimating the activation energy for decomposition kinetics. Two mechanisms of reactions in the azides are illustrated by HN_3 and PbN_6. In the molecule of HN_3 the weak bond is in the azide group, but for PbN_6 the weak bond is the metal-azide bond.

APPENDIX A

ALGORITHM FOR CALCULATING BOND ENERGIES

In the "atoms in molecules" approach to molecular bonding, Moffitt[16] used the atomic electronic energy as the major contribution to the total molecular energy. Ferreira[17] used somewhat the same approach, but considered only the contributions to the molecular bonding energy introduced by the ionization state of the atoms. He assumed that the energy was a continuous and differentiable function of the charge on the atom.

In this paper we follow this assumption, but the function will be derived from energy terms similar to those used by Slater[1] with constants derived from experimental ionization potentials.

$$E_{sj} = -(N + q_j)(A - Bq_j)^2 + NA^2$$

N = Number of valence electrons in the atom

q_j = Excess number of electrons on the atom

A, B = Constants to be determined

The molecular orbitals for the molecule have the form

$$\psi_i = \sum_j c_{ij} \phi_{jk}$$

c_{ij}, constants

ϕ_{jk} an atomic orbital on j'th atom.

It will be assumed that the orbitals are normalized such that

$$\sum_j c_{ij}^2 = 1.$$

Then the number of electrons on an atom is given by

$$n_j = \sum_i c_{ij}^2$$

and the number of excess electrons is given by $q_j = n_j - Z_j$ where

Z_j is the nuclear charge.

The molecular bonding is then[18]

$$E_B = \sum_j E_{sj} + \frac{1}{2} \sum_j \sum_{l \neq j} \frac{q_1 q_1}{R_{j1}} + E_C + \frac{1}{2} \sum_s h\nu_s$$

where:

$$E_C = -\frac{1}{4} \sum_i \sum_j \sum_{l \neq j} \frac{c_{ij}^2 c_{jl}^2 + \sum_k' c_{il} c_{kl} c_{ij} c_{kj}}{R_{il}}$$

$\sum_j$, $\sum_l$ are sums over the atoms

$\sum_i$ is a sum over the valence electrons

$\sum_k'$ is a sum over electrons with same spin as "i" and filling a molecular orbital utilizing the same atomic orbitals as "i"

ν_s is a molecular vibration

R_{j1} is the experimental equilibrium distance between atoms j and l.

It has been found that E_B gives values which are in good agreement with experimental bond energies. When E_B is calculated for a molecule and also for its ionized form, the difference between the two energies gives the ionization potential.

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