Table V. Kinetic Parameters[a] for Structural Conversion of $Ni[(p\text{-}ZC_6H_4)_2MeP]_2X_2$ Complexes[b] in Chloroform Solution

Complex Z, X	$k_t(-50°) \pm 0.5^c$, sec^{-1}	$k_t(25°) \pm 1.0$, sec^{-1}	$\Delta H^\ddagger \pm 4$, kcal/mol	$\Delta S^\ddagger \pm 10$, eu
H, Br	1.1×10^3	8.5×10^5	11	6
Cl, Br	5.2×10^2	3.8×10^5	11	4
OMe. Br	6.8×10^1	1.4×10^5	13	9
OMe, Cl	3.3×10^3	1.6×10^6	10	5

[a] Parameters obtained from a least-squares fit to plot of log k_t/T *vs.* $1/T$ and using the relationship $k_t = \frac{kT}{h}\exp\left[\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right]$.

[b] Complex concentrations are ~0.1 *M*. [c] k_t is the first-order rate constant for the reverse reaction in $P \underset{k_t}{\overset{k_p}{\rightleftharpoons}} T$.

plexes c and d in the figure could not be completely slowed down due to prior freezing of their solutions. This assumption is a reasonable one because transverse relaxation times are expected to be nearly equal for such similar complexes.[48] The calculated τ_t values from eq 7 are insensitive to small changes in $1/T_{2t}'$ due to the rapidly rising behavior of $1/T_{2t}$ when exchange broadening becomes important. The rate constants and kinetic parameters determined from a least-squares fit of eq 8 are set out in Table V.[49]

The principal purpose of the kinetic study has been to demonstrate that the structural interconversion of the present group of $Ni(Ar_2MeP)_2X_2$ complexes, in sharp contrast to all known bischelate Ni(II) systems involved in this process, can be demonstrably slowed down or completely frozen out in chloroform solution at temperatures down to *ca.* −70° as a lower limit. Consequently, a comprehensive study of all of the complexes in Table II has not been performed. From the limited data at hand the order of increasing frequency of structural interchange at parity of phosphine is Br < Cl < I. In no case could an iodide system be frozen out. From this unexpected rate order, which has also been found by LaMar in dichloromethane solutions,[26] it appears that the factors determining the kinetics are complex and involve a combination of steric and electronic effects. Attempts to measure kinetics on several other systems were thwarted by overlapping signals, low concentrations of tetrahedral isomers, and freezing of solutions before reaching the slow exchange region. A full evaluation of kinetic trends must await additional results obtained in solvents of different dielectric constants and lower freezing points.

Acknowledgments. This research was supported by research grants NSF GP-7576X (M. I. T.) and GP-6321 (Princeton University). L. H. P. is the recipient of a National Institutes of Health Postdoctoral Fellowship for 1969–1970. We are indebted to Dr. G. N. LaMar for communication of results prior to publication and for a number of useful discussions.

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(48) The line assumed here for log $(1/T_t')$ *vs.* $1/T$ is similar to that reported for the analogous triphenylphosphine complexes.[32]

(49) The activation parameters in Table V were determined over a small temperature range (typically 30°) and, therefore, are subject to large experimental error. Other methods of kinetic analysis, *e.g.*, use of fast exchange approximations which would extend the temperature range, were not employed due to uncertainties in determining the temperature dependencies of the widths of the planar *m*-H resonances. The experimental errors given in Table V were estimated by assuming an error of ±1 cps in $\Delta\nu_{1/2}$ and ±1° in T and plotting plus and minus extremes of log (k_t/T) *vs.* $1/T$.

Thermodynamic Interpretation of Chemical Shifts in Core-Electron Binding Energies

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Abstract: By making several approximations, it is possible to calculate, from available thermodynamic data, a "thermochemical energy" corresponding to the core-electron binding energy for an atom in a compound. For a given element, such calculated "thermochemical energies" are linearly related to experimental binding energies. Thus it is possible to estimate thermodynamic data from binding energies, and *vice versa*. The principal approximation made in these calculations is that atomic cores which have the same charge are chemically equivalent. The relatively small shifts in core-electron binding energy observed for an atom in a particular cation or anion in a series of salts are explicable in terms of lattice energy considerations.

Atomic core-electron binding energies for solid compounds can be measured by X-ray photoelectron spectroscopy with a precision of ±0.2 eV and, for a given element, have been shown to change as much as 15 eV with changes in chemical environment.[1] The binding energies correlate with the oxidation states of

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(1) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmar, S.-E. Karlsson, I. Lindgren,

the element or, better, with the estimated atomic charges: the higher the effective charge on an atom, the higher the binding energy. This correlation is intuitively reasonable because one would expect that it would be easier for an electron to leave an atom which has a negative charge than one which has a positive charge. Inasmuch as several fairly simple methods are available for estimating atomic charges, correlations of this type are easily made and have been used to infer structural information about compounds.[1-4] However there are at least two deficiencies in the use of these atomic charge–binding energy correlations.

First, in plots of core-electron binding energy *vs.* estimated atomic charge, the points are scattered fairly widely from a smooth curve or straight line, suggesting that there is not an exact one-to-one correspondence between binding energy and atomic charge.[5] The fit of the points in such plots is only slightly improved by using more sophisticated methods for estimating atomic charges. This slight improvement can be seen by comparing the plots of nitrogen 1s binding energies *vs.* nitrogen atom charges calculated by Pauling's method, by an extended Hückel MO method, and by the CNDO method.[1,2,4]

Second, the available approximate methods for estimating atomic charges (including those mentioned above) yield markedly different values. Thus, although a rough correlation can be obtained using charges consistently calculated by any one method, and although that empirical correlation can be very useful in structural studies, one obviously cannot attach fundamental or quantitative significance to "experimental" atomic charges derived from measured binding energies.

In this paper we shall consider several ways of splitting up the X-ray photoelectric process into constituent steps. We shall show that for one of these ways the estimated energies of certain steps correlate closely with the experimental binding energies.

The Inadequacy of the Concept of Fractional Atomic Charge

Let us consider the promotion of a core electron from a particular atom, M, in a crystalline solid to the Fermi level of that solid. Let us assume that we are able to calculate for this atom a charge, z, which in general will be nonintegral. The core-electron binding energy of a *gaseous* atom possessing a charge z is a quantity which is a smooth function of z and which can be estimated fairly accurately.[6] However, this gas-phase binding energy is just one of several energy terms which must be summed in order to evaluate the binding energy for the atom in the solid. The sum of the following processes corresponds to the desired process.

$$\mathrm{M}^{z}(\text{lattice}) \longrightarrow \mathrm{M}^{z}(\mathrm{g}) \tag{1}$$

$$\mathrm{M}^{z}(\mathrm{g}) \longrightarrow \mathrm{M}^{z+1*}(\mathrm{g}) + \mathrm{e}^{-}(\mathrm{g}) \tag{2}$$

$$\mathrm{M}^{z+1*}(\mathrm{g}) \longrightarrow \mathrm{M}^{z+1*}(\text{lattice}) \tag{3}$$

$$\mathrm{e}^{-}(\mathrm{g}) \longrightarrow \mathrm{e}^{-}(\text{Fermi}) \tag{4}$$

$$\mathrm{M}^{z}(\text{lattice}) \longrightarrow \mathrm{M}^{z+1*}(\text{lattice}) + \mathrm{e}^{-}(\text{Fermi}) \tag{5}$$

In these equations, the asterisk indicates that the atom is lacking one core electron, and e⁻(Fermi) refers to an electron at the Fermi energy level in the solid. As we have pointed out, the energy of process 2 is calculable. The energy of process 4 corresponds to the work function of the solid and is a difficult quantity to estimate. Probably the best one can do is to assume (or to hope) that the work function is relatively small and that it does not change much on going from one solid compound to another.

The energies of processes 1 and 3 are large "lattice energies" of a rather unusual type, and at present it is almost a hopeless task to estimate these quantities with an accuracy comparable to that of the experimental binding energies.[7] Fadley, *et al.*,[6] assumed that "lattice energies" of this type could be calculated by considering only coulombic interactions. They essentially adjusted the atomic charges so that the calculated energies for processes 1, 2, and 3 were consistent with the experimental binding energies.

For the atoms of a given element in a random set of compounds (*e.g.*, for the nitrogen atoms in NH_4Cl, $NaNO_2$, pyridine, etc.), these "lattice energies" for processes 1 and 3 are not simply related to the magnitude of z, the charge on the atom. In fact, if one were to find two entirely different compounds in which the nitrogen atoms had almost identical charges, it is probable that the combined energies of processes 1 and 3 would be quite different for the compounds. Thus, although the energy of process 2 correlates with z, there is no reason to except anything better than a rough correlation between the energy of process 5 (the binding energy) and z.

A Scheme Involving Neutral and Integrally Charged Species

Let us now consider another general method for dividing up the process corresponding to the promotion of a core electron to the Fermi level in a solid. In this method the atom in question is either assigned an integral charge or is considered as part of a neutral molecule or an integrally charged ion. We can use the same set of equations (1–5) that was used when considering fractionally charged atoms, except that now z must be zero or a positive or negative integer and now M^z can represent a molecule or ion.

In process 1 we remove the molecule or ion from its site in the crystal lattice. In process 2 the core electron of the atom is question is ejected from the gaseous species. (As before, the asterisk indicates a core-electron hole in the atom.) Then in process 3 we insert the

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and B. Lindberg, "ESCA; Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

[2] J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

[3] R. Nordberg, U. Celius. P. F. Hedén, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, Uppsala University Report UUIP-581, March 1968.

[4] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

[5] Indeed, as will be shown later, there is no reason to expect a smooth correlation between binding energy and atomic charge for solid compounds. A smooth correlation would be expected only for isolated atoms, and in such cases the concept of fractional charge is hypothetical.

[6] C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).

[7] Waddington[8] has shown that uncertainties as great as ±30 kcal/mol are common when estimating the lattice energies of relatively simple binary compounds.

[8] T. C. Waddington, *Advan. Inorg. Chem. Radiochem.*, **1**, 157 (1959).

M^{z+1*} group into the lattice site previously occupied by the M^z group, and in process 4 we place the electron into the Fermi level of the solid. The energy of process 5 is the experimental binding energy.

Our aim is to devise a general method for estimating the energies of the four processes which comprise process 5 in the hope that the sum of these estimated energies is a quantity that correlates well with experimental binding energy for a given element in a series of compounds.

It will be noted that process 4 has exactly the same significance that it had in the preceding scheme for dividing up the X-ray photoelectric process. Again, because of our inability to predict the Fermi energy levels in a wide variety of solids, we are forced to assume that the energy of process 4 (the work function for the substance) does not markedly vary on going from one compound to another. In the following paragraphs we shall describe a general method for estimating the sum of the energies of the three remaining processes (1, 2, and 3). We shall use, as illustrative examples, the processes corresponding to the removal of nitrogen 1s electrons from ammonia and sodium nitrite.

$$\mathrm{NH_3(lattice)} \longrightarrow \mathrm{NH_3^{+*}(lattice)} + \mathrm{e^-(Fermi)}$$

$$\mathrm{NO_2^-(lattice)} \longrightarrow \mathrm{NO_2^*(lattice)} + \mathrm{e^-(Fermi)}$$

Process 1. Our estimate of the energy of process 1 depends on whether M^z is situated in the bulk of the crystal lattice or near the surface. In view of the absorption of X-rays by matter, the X-ray photoelectric process might be expected to occur principally near the surface of the solid. However, Siegbahn, *et al.*,[1] have shown that X-ray photoelectrons are emitted in solids from a surface layer about 100 Å thick. Photoelectron emission is clearly not limited to the outer few ångströms, because if that were the case then the contribution of process 1 to the binding energy would be expected to range from one-half the lattice energy (for transitions at the surface) to almost the full lattice energy (for transitions within the crystal). Consequently the spectra would be expected to consist of broad bands, with half-widths as great as 10 eV. Inasmuch as relatively sharp spectra are actually observed, we believe that most of the transitions occur in the bulk of the crystal.

If M^z is a neutral molecule, the energy of process 1 is twice the sublimation energy of the compound. If M^z is an ion in a crystal lattice with counterions of charge $-z$, the energy of process 1 is the lattice energy of the compound.[9] Therefore we write the following equations for this process for NH_3 and $NaNO_2$.

$$\mathrm{2NH_3(s)} \longrightarrow \mathrm{2NH_3(g)}$$

$$\mathrm{NaNO_2(s)} \longrightarrow \mathrm{Na^+(g)} + \mathrm{NO_2^-(g)}$$

Process 2 and the Concept of "Equivalent Cores." We assume that when the core electron of the atom in question is ejected from the species M^z in process 2, the valence electrons adjust to the increase in charge of the atom's core. (Later we shall consider the justification for this assumption in detail.) Now if we make the approximation that *cores which have the same charge are chemically equivalent*, then we conclude that the increase in the atom's core charge by one unit corresponds to the replacement of the atomic nucleus by a nucleus of the next element in the periodic table. In the particular cases under discussion, the practical result of this approximation is the realization that the radicals NH_3^{+*} and NO_2^* are equivalent to the species OH_3^+ and O_3, respectively, as far as the valence electrons are concerned. On this basis we assume that the energies of the following processes are zero.

$$\mathrm{O^{6+}(g)} + \mathrm{NH_3^{+*}(g)} \longrightarrow \mathrm{N^{6+*}(g)} + \mathrm{OH_3^+(g)}$$

$$\mathrm{O^{6+}(g)} + \mathrm{NO_2^*(g)} \longrightarrow \mathrm{N^{6+*}(g)} + \mathrm{O_3(g)}$$

Thus we may write the following equations for process 2.

$$\mathrm{O^{6+}(g)} + \mathrm{NH_3(g)} \longrightarrow \mathrm{N^{6+*}(g)} + \mathrm{OH_3^+(g)} + \mathrm{e^-(g)}$$

$$\mathrm{O^{6+}(g)} + \mathrm{NO_2^-(g)} \longrightarrow \mathrm{N^{6+*}(g)} + \mathrm{O_3(g)} + \mathrm{e^-(g)}$$

Process 3. When $z = 0$, process 3 corresponds to the condensation of a radical cation into a hole in a lattice of neutral molecules. We shall assume that the energy of this process is unchanged when we replace the cation by the corresponding neutral species. In the case when M^z is NH_3, we write for process 3

$$\mathrm{2NH_3(g)} \longrightarrow \mathrm{2NH_3(s)}$$

When $z = -1$, process 3 corresponds to the condensation of a neutral radical into a hole in an ionic lattice. We shall use the concept of equivalent cores discussed above and shall assume that in process 3 the species M^{z+1*} may be replaced with the appropriate neutral molecule and that the hole in the ionic lattice may be replaced with a hole in the corresponding lattice of neutral molecules. Thus in the case of $NaNO_2$ we assume that the energy of process 3 is the same as that for the condensation of O_3 into a hole in a lattice of solid O_3. We write

$$\mathrm{2O_3(g)} \longrightarrow \mathrm{2O_3(s)}$$

Fortunately the energy of this type of process is not large, and so even this crude approximation does not introduce much error.

When z is other than 0 or -1, it is relatively difficult to estimate the energy of process 3 (and sometimes process 1). For example, consider the ejection of a core electron from sulfur in Na_2S. Here the energy of process 1 (the removal of a sulfide ion from the lattice) is not readily calculable from the lattice energy of Na_2S without a detailed consideration of Madelung energies. The energy of process 3 (the insertion of S^{-*} into a sulfide vacancy in Na_2S) is even more difficult to estimate. Therefore we shall now limit ourselves to compounds where $z = 0$ or -1.

"Thermochemical Energies." By adding the equation corresponding to processes 1, 2, and 3, we obtain the following results for $NH_3(s)$

$$\mathrm{NH_3(g)} + \mathrm{O^{6+}(g)} \longrightarrow \mathrm{OH_3^+(g)} + \mathrm{N^{6+*}(g)} + \mathrm{e^-(g)}$$

and for $NaNO_2(s)$

$$\mathrm{NaNO_2(s)} + \mathrm{O^{6+}(g)} + \mathrm{O_3(g)} \longrightarrow \mathrm{2O_3(s)} + \mathrm{N^{6+*}(g)} + \mathrm{Na^+(g)} + \mathrm{e^-(g)}$$

We may similarly write, for other nitrogen compounds whose X-ray photoelectron spectra have been obtained, the following equations.

$$\mathrm{NaN_3(s)} + \mathrm{O^{6+}(g)} + \mathrm{N_2O(g)} \longrightarrow \mathrm{2N_2O(s)} + \mathrm{N^{6+*}(g)} + \mathrm{Na^+(g)} + \mathrm{e^-(g)}$$

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(9) This statement is strictly true only for lattices in which interchange of the cations and anions yields an indistinguishable lattice, but this is a characteristic of most MX lattices.

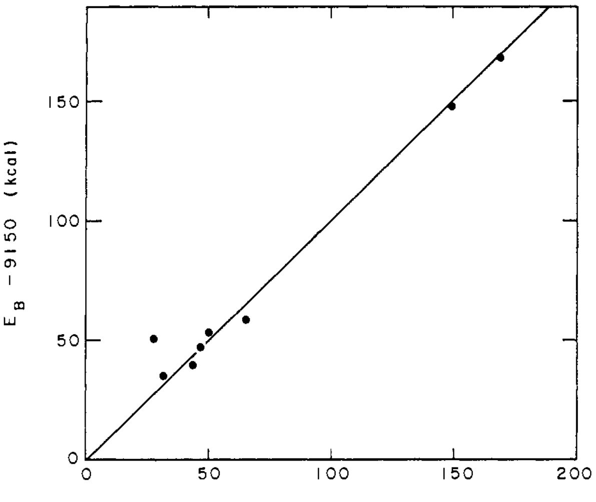

Figure 1. Nitrogen ls binding energies (E_B) *vs.* the corresponding thermochemical energies (E_T). The E_B and E_T values have been reduced by 9150 and 96 kcal/mol, respectively. to make the best straight line pass through the origin.

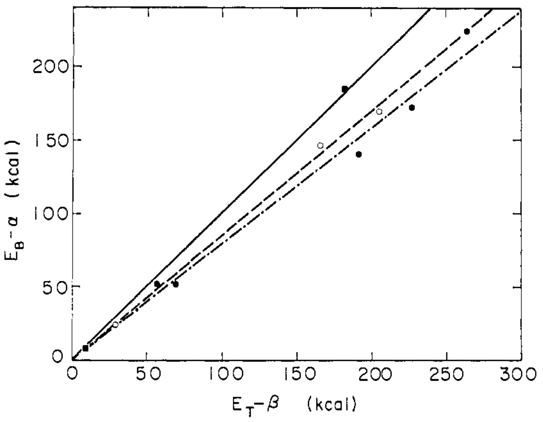

Figure 2. Core-electron binding energies (E_B) *vs.* thermochemical energies (E_T). The squares correspond to boron compounds (α = 4314, β = 157). the filled circles correspond to carbon compounds (α = 6544. β = 90), the open circles correspond to iodine compounds ($\alpha = -24, \beta = 165$).

$$KOCN(s) + O^{6+}(g) + CO_2(g) \longrightarrow 2CO_2(s) + N^{6+*}(g) + K^+(g) + e^-(g)$$

$$KCN(s) + O^{6+}(g) + CO(g) \longrightarrow 2CO(s) + N^{6+*}(g) + K^+(g) + e^-(g)$$

$$KSCN(s) + O^{6+}(g) + SCO(g) \longrightarrow 2SCO(s) + N^{6+*}(g) + K^+(g) + e^-(g)$$

We shall refer to the preceding six reactions as *thermoequivalent* reactions, because they are supposed to be thermodynamically equivalent to the core-electron emission processes for the compounds on the left sides of the equations. It will be noted that the energies of these thermoequivalent reactions can, in principle, be evaluated from thermodynamic data. Inasmuch as the species $N^{6+*}(g)$ and $O^{6+}(g)$ appear in all these reactions, the energies of formation of these species contribute equally to the energies of the reactions. Consequently *differences* in the energies of the reactions are unaffected by ignoring the species $O^{6+}(g)$ and $N^{6+*}(g)$, and we have done so for simplicity in calculation. We shall refer to the simplified calculated energies as *thermochemical energies*, E_T. These energies and the corresponding experimental 1s binding energies for nitrogen compounds are presented in Table I. The data, when plotted as in Figure 1, clearly show that the binding energy, E_B, is a linear function of the thermochemical energy, E_T. The scatter of the points is considerably less than that found in plots of E_B against estimated nitrogen atom charges.[2,4] In fact, inasmuch as the slope of the straight line in Figure 1 is unity, we may state that changes in E_T are equal to corresponding changes in E_B.

Table I. Nitrogen 1s Binding Energies (E_B) and the Corresponding Thermochemical Energies (E_T)

Compound	E_B, kcal/mol	E_T, kcal/mol[a]
$NaNO_2$	9318	261
$AgNO_2$	9305	284
KNO_2	9298	240
Na[N-N-N]	9208	150[b]
NaCN	9203	138
KCN	9201	120
NH_3	9196	151[b]
KSCN	9189	128
KOCN	9185	115

[a] E_T values were calculated from data in ref 22 except where otherwise indicated. [b] See Calculations section.

Extension to Other Elements. Similar calculations can be carried out for the compounds of other elements for which both X-ray photoelectric data and the appropriate thermodynamic data are available. However, the number and reliability of the data are not as great as in the case of nitrogen compounds. For carbon compounds, we may write the following thermoequivalent reactions.

$$CH_4(g) + N^{5+}(g) \longrightarrow NH_4^+(g) + C^{5+*}(g) + e^-(g)$$

$$NaHCO_3(s) + N^{5+}(g) + HNO_3(g) \longrightarrow Na^+(g) + 2HNO_3(s) + C^{5+*}(g) + e^-(g)$$

$$NaCH_3CO_2(s) + N^{5+}(g) + CH_3NO_2(g) \longrightarrow Na^+(g) + 2CH_3NO_2(s) + C^{5+*}(g) + e^-(g)$$

$$KCN(s) + N^{5+}(g) + N_2(g) \longrightarrow K^+(g) + 2N_2(s) + C^{5+*}(g) + e^-(g)$$

$$CO_2(g) + N^{5+}(g) \longrightarrow NO_2^+(g) + C^{5+*}(g) + e^-(g)$$

For boron compounds we may write the following thermoequivalent reactions.

$$NaBH_4(s) + C^{4+}(g) + CH_4(g) \longrightarrow Na^+(g) + 2CH_4(s) + B^{4+*}(g) + e^-(g)$$

$$NaBF_4(s) + C^{4+}(g) + CF_4(g) \longrightarrow Na^+(g) + 2CF_4(s) + B^{4+*}(g) + e^-(g)$$

And for iodine compounds we may write the following thermoequivalent reactions.

$$KI(s) + Xe^{8+}(g) + Xe(g) \longrightarrow K^+(g) + 2Xe(s) + I^{8+*}(g) + e^-(g)$$

$$KIO_3(s) + Xe^{8+}(g) + XeO_3(g) \longrightarrow K^+(g) + 2XeO_3(s) + I^{8+*}(g) + e^-(g)$$

$$KIO_4(s) + Xe^{8+}(g) + XeO_4(g) \longrightarrow K^+(g) + 2XeO_4(s) + I^{8*}(g) + e^-(g)$$

Values of E_B and E_T for compounds of boron, carbon, and iodine are listed in Table II. In Figure 2, we have plotted $E_B - \alpha$ against $E_T - \beta$, where α and β are arbitrary constants for each element, chosen such as to make the points fall on a line passing through the origin. It can be seen that E_B is a linear function of E_T for the compounds of Table II. Except for the boron-

Table II. Core-Electron Binding Energies (E_B) and the Corresponding Thermochemical Energies (E_T) for Compounds of Boron, Carbon, and Iodine

Compound	E_B, kcal/mol	E_T, kcal/mol[c]
$NaBF_4$	4499[a]	339[d]
$NaBH_4$	4321[a]	170
CO_2	6745[a]	355[d]
$NaHCO_3$	6692[a]	317
$NaCH_3CO_2$	6660[a]	281
CH_4	6572[a]	160[d]
KCN	6572[a]	147
KIO_4	145[b]	370
KIO_3	122[b]	330
KI	0[b]	194

[a] 1s electron binding energies. [b] Weighted average shifts for the core levels. Data from ref 6. [c] E_T values were calculated from data in ref 22 except where otherwise indicated. [d] See Calculations section.

Table III. Values of E_B (1s) and E_T' for Some Nitrogen and Carbon Compounds

Compound	E_B, kcal/mol	E_T' kcal/mol
NH_3	9196	234
NaCN	9203	269
$NaNO_2$	9318	230
$NaNO_3$	9395	255
CH_4	6572	300
KCN	6572	252
C_2H_6	6572	269
CS_2	6623	233
CH_2O	6639	251
CO_2	6745	318
CCl_4	6752	264

compound line, the lines through the points have slopes less than unity. However, perhaps the deviations from unit slope are insignificant in view of the paucity and relative inaccuracy of the data.

Electronic Relaxation

Lifetime of Core-Electron Hole. In the preceding discussion, we have assumed that a measured binding energy corresponds to the formation of an excited state in which a core electron has been removed from an atom. In other words, we have assumed that the X-ray photoelectric transition occurs in a time interval shorter than the lifetime of the core electron hole. This assumption seems plausible because the photoelectric process is believed to occur in a time interval around 10^{-18} sec, whereas X-ray states have lifetimes around 10^{-16} sec.[10] However, we can actually test the assumption using thermodynamic data. If the binding energies corresponded to the formation of a state in which a valence electron had fallen into the core-electron hole, the radical formed would be of a type relatively familiar to chemists. Processes 1, 2, and 3 could be used to obtain a thermoequivalent reaction, but the asterisk would no longer have any meaning. The species X^{z+1*} would refer to the radical in its ground state, and it would no longer be appropriate to apply the concept of equivalent cores. For the nitrogen 1s binding energies in $NaNO_2$(s), $NaNO_3$(s), NaCN(s), and NH_3(s), we write the following reactions.

$$NaNO_2(s) + NO_2(g) \longrightarrow 2NO_2(s) + Na^+(g) + e^-(g)$$
$$NaNO_3(s) + NO_3(g) \longrightarrow 2NO_3(s) + Na^+(g) + e^-(g)$$
$$NaCN(s) + CN(g) \longrightarrow 2CN(s) + Na^+(g) + e^-(g)$$
$$NH_3(g) \longrightarrow NH_3^+(g) + e^-(g)$$

The calculated (or estimated) energies for these four reactions (which we shall call E_T' values) and a set of seven similarly calculated E_T' values for carbon compounds (carbon 1s binding energies) are given in Table III together with the corresponding E_B values. It is clear from these data that the measured binding energies do not correspond to the formation of ground-state radicals with complete cores. First, the E_B and E_T' values in Table III are of an entirely different order of magnitude. In order to make the E_T' values consistent with the E_B values it would be necessary to make the incredible assumption that the work functions (process 4) have values of several thousand kcal/mol. Second, there is no correlation whatsoever between the E_B and E_T' values, as was found between the E_B and E_T values.

Valence Electron Relaxation. Although it is easy to show that an observed binding energy corresponds to the formation of a species lacking a core electron, it is considerably more difficult to show that the valence electrons have relaxed—that is, that they have adjusted to the increased core charge.

It will be remembered that when we calculated the E_T values, it was assumed that the valence electrons were relaxed. Consequently the fact that we observe the linear relationships between E_B and E_T shown in Figures 1 and 2 means that any unreleased electronic relaxation energy must be a linear function of E_B. In fact, because the line of Figure 1 has a slope of unity, any unreleased relaxation energy for nitrogen compounds must be a constant. These restrictions on the relaxation energy seem sufficiently improbable to us that we feel our assumption of complete relaxation is confirmed. However we have further confirmation in the form of estimated electronic relaxation energies. We have used the CNDO method to calculate the differences in the total valence electron energies for the following pairs of gaseous species: N_3^- and N_3^*, CN^- and CN^*, OCN^- and OCN^*, and NO_2^- and NO_2^*. The results were 482, 544, 641, and 773 kcal/mol, respectively.[11] When the E_T values for NaN_3, NaCN, KOCN, and $NaNO_2$ are increased by these relaxation energies, they are no longer linearly related to the corresponding E_B values.

According to Koopmans' theorem[12] an E_B value should correspond to the formation of an excited state with unrelaxed electrons. In Table IV we give, for a variety of species, the E_B values and the corresponding negative core electron energies ($-\epsilon$) obtained from *ab initio* calculations. If Koopmans' theorem were valid in this situation, the E_B and $-\epsilon$ values would be equal. In fact, the E_B values are consistently smaller than the $-\epsilon$ values, and the differences (given in the third column

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(10) L. G. Parratt, *Rev. Mod. Phys.*, 31, 616 (1959).

(11) A modified CNDO/1 version involving empirically evaluated repulsion integrals was used, as per P. M. Kuznesof and D. F. Shriver, *J. Amer. Chem. Soc.*, 90, 1683 (1968). Calculations were completed for each anion using the normal input parameters and also using contracted nitrogen 2s and 2p orbitals (the shielding parameter was decreased by 0.85, which is equivalent to removing the shielding of one nitrogen 1s electron). The difference in the total valence electron energies for these two cases is our estimated electronic relaxation energy. Neglect of core electron relaxation energies and changes in the valence electron bonding parameters and one-center kinetic and potential energies make this estimate very approximate.

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Table IV. E_B Values and the Corresponding *Ab Initio* Calculated Energies for 1s Electrons

Compound[a]	E_B, kcal/mol	$-\epsilon$, kcal/mol	$-\epsilon - E_B$, kcal/mol
CH_4	6572	7033[b]	461
CF_3H	6805	7374[b]	569
CO_2	6745	7181[c]	436
C_2H_6	6572	7036[d]	464
H_2CO	6639	7123[e]	484
C_5H_5N	9178	9837[f]	659
NH_3	9196	9717[g]	521
KCN	6572	6844[h]	272
KCN	9201	9556[h]	355
Na(NNN)	9309	9706[i]	397
Na(NNN)	9208	9549[i]	341
KSCN	9189	9607[c]	418
KOCN	9185	9579[c]	394

[a] The energies refer to the 1s electrons of the atoms indicated in boldface type. [b] T.-K. Ha and L. C. Allen. *Int. J. Quantum Chem. Symp.*, **1**, 199 (1962). [c] A. D. McLean and M. Yoshimine. "Tables of Linear Molecule Wave Functions," International Business Machines Corp., 1967. [d] E. Clementi and D. R. Davis, *J. Chem. Phys.*, **45**, 2593 (1966). [e] R. J. Buenker and J. L. Whitten in "Compendium of *Ab Initio* Calculations of Molecular Energies and Properties," M. Krauss. Ed.. National Bureau of Standards Technical Note 438, U. S. Government Printing Office, Washington, D. C.. 1967. [f] E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967). [g] P. Rajagopal, *Z. Naturforsch.. A*, **20**, 1557 (1965). [h] D. N. Hendrickson and P. M. Kuznesof. *Theor. Chim. Acta*. in press. [i] S. D. Peyerimhoff and R. J. Buenker. *J. Chem. Phys.*. **47**, 1953 (1967).

Table V. A Comparison of Relative Values of E_B and E_T for Nitrates, Nitrites, and Cyanides

Salt	Relative[a] E_B, kcal	Relative[a] E_T, kcal
$LiNO_3$	+8	+32
$NaNO_3$	0	0
KNO_3	−5	−7
NH_4NO_3	−6	−18
$AgNO_3$	−14	+26
$NaNO_2$	0	0
KNO_2	−26	−20
$AgNO_2$	−19	+23
NaCN	0	0
KCN	−2	−18

[a] Relative to the sodium salts.

of Table IV) are of the same magnitude as the values that we estimated for electronic relaxation energies.

Orientational Excitation Energy

Although measured core-electron binding energies correspond to the formation of species in which the valence electrons have probably relaxed, we believe (on the basis of the Born–Oppenheimer approximation) that the atoms in these species have not relaxed with respect to their relative positions. For example, we assume that the nitrogen 1s binding energy of cyanide ion corresponds to the formation of a CN* radical with the same C–N bond distance as in the ground state of the cyanide ion (1.14 Å). From the potential energy data for carbon monoxide[13] (r_{eq} = 1.128 Å), we estimate the unreleased excitation energy to be about 1 kcal/mol. From the potential energy data for molecular nitrogen[14] (r_{eq} = 1.098 Å), we estimate the excitation energy associated with the carbon 1s binding energy of cyanide to be about 3 kcal/mol. If the orientational excitation energies associated with all other core-electron binding energies are of the same general magnitude as these estimated values, *i.e.*, 1–3 kcal/mol, then the error we have made by ignoring these excitation energies is less than the precision of the E_B values and is negligible.

Lattice Shifts

Anions. According to the approximate methods discussed previously, the binding energies for an atom in a particular −1 anion in a series of salts should differ only by the differences in the contributions from process 1, *i.e.*, by the differences in the energy required to remove the anion from the lattice. In the case of salts with +1 cations, these differences should be equal to the differences in the lattice energies of the salts. Some idea of the accuracy of this postulate can be obtained from Table V, where E_B and E_T values for nitrates, nitrites, and cyanides (all *relative* to the sodium salts) are tabulated. The several marked discrepancies between the E_B and E_T values might suggest that the postulate has no value. However, we believe that, except for the case of KCN, the large discrepancies can be rationalized in terms of possibly spurious E_B values. The tabulated E_B value for $LiNO_3$ may be low because of hydration of the sample ($LiNO_3$ is very hygroscopic). Hydration of the lithium ions would be expected to make it easier to remove an anion from the lattice. The E_B values for $AgNO_3$ and $AgNO_2$ may be low because of decomposition of the samples in the X-ray beam. These samples, contrary to the others, became colored upon irradiation. We have no explanation for the large discrepancy in the case of KCN. We believe the data of Table V indicate that, for a series of similar salts, the work function (the energy of process 4) usually does not vary by more than 10 kcal/mol.

In the case of salts with cations having charges greater than +1, the estimation of the energy of process 1 is considerably more complicated. Consider the nitrogen 1s binding energy of a nitrate of a +2 metal ion. The energy of removing a nitrate ion from an $M(NO_3)_2$ lattice is some fraction f of the energy of removing an M^{2+} ion and two NO_3^- ions from the lattice. The latter energy can be calculated from thermodynamic data (it is twice the lattice energy), but f is a quantity whose evaluation requires detailed structural information. We have used binding energies and thermodynamic data for a series of +2 metal nitrates to calculate *empirical* values of f. These data are presented in Table VI. The values of f are remarkably similar; the average value is 0.159 ± 0.013. The value of f can be estimated for the fluoride ion in calcium fluoride if we make the reasonable assumption that the removal energies for F^- and Ca^{2+} partition in the same ratio as the

Table VI. Nitrogen 1s Binding Energies for Nitrates of 2+ Metal Ions and Empirically Evaluated f Values

Salt	E_B, kcal/mol	f
$Mg(NO_3)_2$	9408	0.155
$Ca(NO_3)_2$	9406	0.170
$Ba(NO_3)_2$	9399	0.180
$Cd(NO_3)_2$	9378	0.130
$Pb(NO_3)_2$	9395	0.160

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(13) I. Tobias, R. J. Fallon, and J. T. Vanderslice, *J. Chem. Phys.*, **33**, 1638 (1960).

(14) S. Flügge, P. Walger, and A. Weiguny, *J. Mol. Spectrosc.*, **23**, 243 (1967).

corresponding electrostatic energies. If we systematically delete half of the fluoride ions in CaF_2 and change the charge on the remaining fluoride ions to -2, we are left with a pseudo-zinc-blende structure.[15,16] Now the energy of removing a Ca^{2+} ion from CaF_2 is equal to the energy of removing a Ca^{2+} ion from the pseudo-zinc-blende structure, and this energy is equal to the lattice energy of the pseudo-zinc-blende structure.[9] Inasmuch as the lattice energies of the two structures are proportional to the Madelung constants[17] times the product of the ionic charges, we may calculate the quantity $1 - 2f$ for CaF_2 as $1 - 2f = 1.638/2.519 = 0.650$. Thus we calculate $f = 0.175$ for the fluoride ion in CaF_2. The value is sufficiently close to the value empirically found for various $M(NO_3)_2$ salts to suggest that it may be used as a rough value for any MX_2 salt. The method has limited applicability to the calculation of E_T values, however, because it requires the knowledge of the heats of formation of gaseous anions (which generally are known very inaccurately).

Potassium Salts. Potassium core-electron binding energies have been determined for a variety of potassium salts; the results are given in the second column of Table VII. Probably the most remarkable feature of these binding energies is the fact that they are essentially constant on going from one salt to another. For the potassium halides, we can use an approximate method for estimating the sum of the energies of processes 1 and 3. The energy of process 1 is simply the lattice energy of the salt, U. The energy of process 3 is the energy of inserting a K^{2+*} ion (or, using the concept of equivalent cores, a Ca^{2+} ion) into a cation vacancy in the potassium salt. We assert that the energy of process 3 may be closely approximated by the Coulomb lattice energy[18] ($-2U_c$) plus the energy of interaction of the K^{2+} ion with the dipoles induced in the surrounding halide ions ($-U_p$). We have estimated $-U_p$ using the known polarizabilities of the halide ions and the assumption that the only charge-dipole forces of consequence are those between the K^{2+*} ion and six halide ions octahedrally arranged with a K^{2+*}-X^- distance equal to the normal K^+-X^- distance in the salt.[19] The calculated values of $U - 2U_c - U_p$ are given in the third column of Table VII; it can be seen that the values are essentially constant. Thus the near constancy of the experimental E_B values is in accord with theory. In fact if our values of $U - 2U_c - U_p$ are an accurate measure of the sum of the energies of processes 1 and 3, we may ascribe the observed variations in E_B for potassium salts to variations in the energy of process 4, the work function.

Table VII. Potassium 3p Binding Energies and Some Values of $U - 2U_c - U_p$[a]

Salt	E_B	$U - 2U_c - U_p$
KI	399	-298
KBr	374	-304
KCl	385	-301
KF	418	-301
KCN	392	
KNO_3	401	
KNO_2	393	
KOCN	396	

[a] Values in kcal/mol.

The Prediction of Heats of Reaction

Suppose that a core-electron binding energy is known for an atom in a compound, but that it is not possible to calculate the corresponding thermochemical energy because the heat of formation of one of the species in the thermoequivalent reaction is unknown. If a linear correlation between E_B and E_T has already been established for the element, one can estimate the E_T value using the correlation and then estimate the heat of formation of the species whose heat of formation is unknown.

For example, from the known 1s binding energy of the middle nitrogen atom in sodium azide (9309 kcal/mole) and Figure 1, we estimate $E_T = 249$ kcal/mole for the following thermoequivalent reaction.

$$NaN_3(s) + NON(g) + O^{6+}(g) \longrightarrow 2NON(s) + Na^+(g) + N^{6+*}(g) + e^-(g)$$

By estimating the sublimation energy of NON to be the same as that of CO_2, and by using the known heats of formation of $NaN_3(s)$ and $Na^+(g)$, we calculate $\Delta H_f° = 120$ kcal/mol for NON(g). From this we calculate that $\Delta H° = -100$ kcal/mol for the isomerization $NON(g) \rightarrow NNO(g)$.

The heats of formation of various hydrogen-containing gaseous cations can be estimated from E_B data, and these can be used to calculate proton affinities. For example, from the carbon 1s binding energy of chloroform (6683 kcal/mol) and Figure 2 we estimate $E_T = 265$ kcal/mol for the following thermoequivalent reaction.

$$CHCl_3(g) + N^{5+}(g) \longrightarrow NHCl_3^+(g) + C^{5+*}(g) + e^-(g)$$

By combining this with the known heat of formation of gaseous chloroform we calculate $\Delta H_f° = 240$ kcal/mol for $NHCl_3^+(g)$. When the latter quantity is combined with the heats of formation of $H^+(g)$ and $NCl_3(g)$, we obtain 190 kcal/mol for the proton affinity of NCl_3.

$$NCl_3(g) + H^+(g) \longrightarrow HNCl_3^+(g) \qquad \Delta H° = -190 \text{ kcal/mol}$$

We have similarly calculated proton affinities for other species. These estimated values, as well as literature values for ammonia and water, are presented in Table VIII.

When thermodynamic data are available for the calculation of an E_T value for a compound for which no E_B value is known, it is possible to predict the E_B value. For example, we may write the following thermoequivalent equation for sodium amide (nitrogen 1s binding energy).

$$NaNH_2(s) + O^{6+}(g) + H_2O(g) \longrightarrow 2H_2O(s) + Na^+(g) + N^{6+*}(g) + e^-(g)$$

Available thermochemical data yield $E_T = 93$ kcal/mol; from Figure 1 we then predict the nitrogen 1s binding energy in sodium amide to be 9153 kcal/mol.

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(15) This fact was pointed out to us by Professor D. H. Templeton. It is also discussed by Wells.[16]

(16) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, pp 119–121.

(17) The Madelung constants for zinc-blende and CaF_2 are 1.638 and 2.519, respectively.

(18) The coulombic energy for inserting a 2+ ion in a lattice is twice that for inserting a 1+ ion in the same lattice.

(19) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 62.

Table VIII. Gas-Phase Proton Affinities Estimated from Core-Electron Binding Energy Data

Compound	Proton affinity, kcal/mol
C_5H_5N	247
CH_3NH_2	247
CH_3CONH_2	239
NH_3	214[a]
CH_3NO_2	209
NH_2OH	208
n-C_4H_9OH	202
C_6H_5OH	192
NCl_3	190
H_2O	169[b]
NF_3	133

[a] Proton affinity taken from ref 26. [b] Proton affinity taken from ref 24.

Core-Electron Binding Energies

Most of the core-electron binding energies were taken from the literature.[20] The carbon 1s binding energy of CHF_3 (6768 kcal/mol) was recently determined by Professor Darrah Thomas, to whom we are grateful for this privileged information. Nitrogen 1s binding energies for $LiNO_3$, KNO_3, $AgNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, KNO_2, $AgNO_2$, and NaCN, potassium 3p binding energies for KF, KCl, KBr, KI, KNO_3, KNO_2, KOCN, and KCN, and boron 1s binding energies for KBH_4 and $NaBF_4$ were determined by us using Mg Kα X-radiation (1253.6 eV) and an iron-free double-focusing magnetic spectrometer of 50-cm radius.[21] A detailed description of the experimental aspects of X-ray photoelectron spectroscopy can be found in the review by Siegbahn, *et al.*[1] The binding energy for each compound was measured at least three times. The carbon 1s line (arising from the film of pump oil on each sample) served as a convenient reference peak. The work function of the spectrometer material (aluminum) was assigned the value 4.0 eV. Powdered samples were mounted on an aluminum plate by means of double-faced conducting adhesive tape.

Calculations

Most of the thermodynamic data were taken from U. S. National Bureau of Standards publications.[22] However, some data were obtained from other sources. Heats of formation for the following compounds were taken from, or calculated from data in, the indicated references: NaN_3,[23] $H_3O^+(g)$,[24] $NaBF_4$,[23] $CF_4(g)$,[25] $NH_4^+(g)$,[26] $NO_2^+(g)$,[27] $NaBH_4$,[28] XeO_3,[29] $XeO_4(g)$,[29] $CH_3COCH_3(g)$,[30] $CH_3CONH_2(g)$,[31] $CH_3CO_2H(g)$,[32] $CHF_3(g)$,[28] *n*-$C_4H_9NH_2(g)$,[33] $C_6H_5NH_2(g)$,[34] $NaNH_2$,[35] CN(g),[36] $NO_3(g)$,[37] $C_5H_5N(g)$,[38] $C_6H_6(g)$,[39] *n*-$C_4H_9OH(g)$,[40] and $NO_3^-(g)$.[8] Ionization potentials for carbon compounds were taken from the compilation of Kiser.[41] In some cases heats of vaporization were estimated using Trouton's rule. Occasionally heats of sublimation were estimated by analogy; for example, the heat of sublimation of XeO_3 was assumed to be the same as that of $AsCl_3$.

The detailed calculations of nitrogen E_T values for $NH_3(s)$ and $NaNO_2(s)$ are given as examples. The thermoequivalent reaction for $NH_3(s)$ is

$$NH_3(g) + O^{6+}(g) \longrightarrow OH_3^+(g) + N^{6+*}(g) + e^-(g)$$

The standard heats of formation at 25° of $NH_3(g)$, $H_2O(g)$, $H^+(g)$, and $e^-(g)$ are -11.0, -57.8, 367.2, and 0 kcal/mol, respectively,[22] and the proton affinity of H_2O is 169 kcal/mol.[24] From these data we calculate, for the thermochemical energy, $E_T = -169 - 57.8 + 367.2 + 11.0 = 151$ kcal/mol. The thermoequivalent reaction for $NaNO_2(s)$ is

$$NaNO_2(s) + O^{6+}(g) + O_3(g) \longrightarrow 2O_3(s) + N^{6+*}(g) + Na^+(g) + e^-(g)$$

The standard heats of fomation at 25° $NaNO_2(s)$, $O_3(g)$, $Na^+(g)$, and $e^-(g)$ are -85.9, 34.0, 145.9, and 0 kcal/mol, respectively, and the sublimation energy of O_3 is 2.6 kcal/mol.[22] From these data we calculate $E_T = -2 \times 2.6 + 34.0 + 145.9 + 85.9 = 261$ kcal/mol.

The calculation of the $U - 2U_c - U_p$ values of Table VII is illustrated for the case of potassium iodide. From the heats of formation of KI(s), $K^+(g)$, and $I^-(g)$ (-78.3, 123.0, and -47.0 kcal/mol, respectively[22]) we calculate $U = 154.3$ kcal/mol. From the K–I distance in crystalline KI (3.526 Å)[42] we calculate, using the Madelung expression, $U_c = 164.6$ kcal/mol. The polarization energy, U_p, is calculated from the following expression for a cation of charge q surrounded octahedrally at a distance r by six ions of polarizability α[19]

$$U_p = \frac{6q\mu_i}{r^2} - \frac{6(1.19)\mu_i^2}{r^3} - \frac{6\mu_i^2}{2\alpha}$$

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(20) Binding energies for the following elements were obtained from the indicated references: nitrogen,[1,2,4] carbon,[3] iodine.[6]

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(22) U. S. National Bureau of Standards Technical Notes 270-1 and 270-2, U. S. Government Printing Office, Washington, D. C., 1965 and 1966; U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

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(28) "JANAF Thermochemical Tables," prepared by the Joint Army-Navy-Air Force Thermochemical Panel under the Advanced Research Projects Agency Program, U. S. Air Force.

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(41) R. W. Kiser, "Introduction to Mass Spectrometry and its Application," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.

(42) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 357.

where μ_i is defined as follows.

$$\mu_i = \frac{\alpha q}{r^2 + 2.37\alpha/r}$$

By substituting $q = 2$, $\alpha = 6.45 \times 10^{-24}$ cm^3,[43] and $r = 3.526$ Å, we obtain $U_p = 123.5$ kcal/mol. Hence $U - 2U_c - U_p = -298$ kcal/mol.

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(43) J. A. A. Ketelaar, "Chemical Constitution," 2nd ed, Elsevier Publishing Co., Amsterdam, 1958, p 91.

Fermi Contact Shifts in Ion Pairing Systems

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Abstract: ^{14}N isotropic resonance shifts have been observed for a tetrabutylammonium cation ion paired to several paramagnetic anionic transition metal complexes. The observed shifts substantiate a Fermi contact interaction between the unpaired electrons of the anion and the cation. This requires that there be some type of weak covalent interaction between the cation and anion in the ion pair. Possible mechanisms by which unpaired spin could be delocalized onto the cation are discussed.

There have been several reports over the past few years dealing with proton isotropic resonance shifts in paramagnetic ion pairing systems.[2–9] Most of the systems which have been studied involve the ion pairing of a tetraalkylammonium cation with some anionic paramagnetic transition metal complex. The observed isotropic resonance shifts for protons on the diamagnetic cations have been interpreted as arising solely from a "pseudocontact" shift; that is, from a direct dipolar coupling between the magnetic moment of the unpaired electrons on the metal and the magnetic moment of the nucleus with which one is concerned. The reason for this is that the alternative mechanism contributing to the isotropic resonance shift, the Fermi contact interaction, would require some kind of covalent bonding between the cation and the anion. The assumption that this latter mechanism is completely negligible seems quite reasonable at first glance; however, we shall present evidence below which, in fact, demonstrates that some unpaired spin density is actually transferred to the cation.

Equation 1 is a general form which describes the

$$(\Delta\nu/\nu_0)_i = -\frac{\beta^2 S(S+1)}{45kT} f(g)\left(\frac{3\cos^2\theta_i - 1}{R_i^3}\right) \quad (1)$$

"pseudocontact shift.[10] $\Delta\nu = \nu_{\text{paramagnetic}} - \nu_{\text{diamagnetic}}$ is the resonance shift for the ith nucleus in the paramagnetic complex referenced to an analogous diamagnetic complex. ν_0 is the rf frequency at which the experiment is carried out. S is the total spin quantum number. R_i is the length of the vector from the metal atom to the ith nucleus and θ_i is the angle between this vector and the principal axis of the paramagnetic molecule or ion. $f(g)$ is some function of the components of the **g** tensor. In the cases with which we will be concerned, *i.e.*, for an axial system and for $\tau_c \gg T_1$ where τ_c and T_1 are the molecular correlation and electron spin relaxation times, respectively, $f(g) = (3g_{\parallel} + 4g_{\perp})(g_{\parallel} - g_{\perp})$.[10b] The important thing to notice in eq 1 is that the pseudocontact shift depends on the anisotropy of the g tensor and on a geometric factor, $(3\cos^2\theta_i - 1)/R_i^3$. In order for the anisotropy in g to be nonzero, the paramagnetic metal atom must be in an environment of noncubic symmetry. Sometimes this results from the geometry of the complex and sometimes it can arise from the ion pairing itself even though the metal ion might otherwise be expected to be in a cubic environment.[9] It can also be seen in eq 1 that as one goes from one nucleus to another in a particular complex or even if the nucleus varies from ^{1}H to ^{13}C to ^{14}N the only term which varies is the geometric factor. This point will be relevant to the results given below.

Larson and Wahl[2] have examined the proton isotropic resonance shifts of tetraalkylammonium cations in aqueous solutions containing paramagnetic $Fe(CN)_6^{3-}$ anions. The observed upfield shifts were considered to be due to a pseudocontact mechanism and the results were used to draw conclusions about the extent of ion pairing in the systems studied. LaMar[4,5] has investigated the proton nmr of the tetrabutylammonium cation in the paramagnetic complexes $[Bu_4N][(Ph_3P)MI_3]$ where M = Co(II) and Ni(II). Once again the shifts were interpreted as arising solely from a pseudocontact interaction with the unpaired electrons on the metal. In this work a geometry for the ion pair ($[Bu_4N][(Ph_3P)MI_3]$) was determined using the observed shifts for the H_1 and H_2 protons[11] in the butyl chains and the calculated geometric factors for these protons.

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(11) The numbering system for the butyl chain will be that used in ref 4, 5, and 9 and is as follows: $N(C_1-C_2-C_3-C_4)_4^+$.