down of this qualitative rule. Its small intensity could be rationalized by the presence of one or more BH_2 groups in B_3H_7.[37]

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CONTRIBUTION FROM THE SCHOOL OF CHEMICAL SCIENCES,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

X-Ray Photoelectron Spectra and Molecular Orbital Interpretation of the Valence Region of Cyanide and Nitrate

BY WILLIAM H. MORRISON, JR., AND DAVID N. HENDRICKSON*

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X-Ray photoelectron spectra were determined for KNO_3 and NaCN in the valence region of 0–40 eV binding energy. In the case of KNO_3, four nonpotassium peaks (26.27, 14.59, 11.56, and 7.46 eV) and two potassium peaks (K_{3s}, 33.40 eV; K_{3p}, 17.37 eV) were detected. In the case of NaCN, five nonsodium peaks (24.67, 16.98, 12.76, 8.96, and 5.28 eV) and one sodium peak (Na_{2p}, 30.52 eV) were found. Extended Hückel, CNDO, and INDO molecular orbital calculations were carried out on nitrate and cyanide and an *ab initio* MO calculation was completed for cyanide. Peak assignments were advanced on the basis of these MO calculations.

Introduction

Inorganic applications of X-ray photoelectron spectroscopy (XPS)[1] have been mainly in the area of studying core-electron binding energies. Chemical shifts of core-electron binding energies have been noted for a large number of elements, and for many of these elements correlations have been established between the core-electron binding energies and atomic charges calculated by molecular orbital treatments (*e.g.*, nitrogen,[2,3] phosphorus,[4,5] boron,[6] and iron[7]). In some cases structural information has been inferred from these correlations.

Recently XPS has been used to study the valence region of various molecules in the gas phase.[8] The observed peaks in the XPS spectra of these gaseous samples have, in many cases, been assigned to the photoionization of electrons from filled molecular orbitals. Interesting comparisons have been made between XPS and ultraviolet photoelectron spectroscopy data for some molecules. Very recently Prins and Novakov[9] reported the XPS valence region (*i.e.*, 0–40 eV binding energy) spectra of *solid* samples of many different perchlorate and sulfate salts. They were able to assign the observed noncation peaks to the photoionizations of electrons from the filled molecular orbitals of the anions. In this paper we report the results of a similar study of salts of nitrate and cyanide.

Experimental Section

Magnesium Kα X-radiation was used to excite the photoelectrons whose energies were analyzed using the Berkeley magnetic-focusing spectrometer. The powdered samples were deposited on double-faced adhesive tape; peak positions were measured *vs.* the C_{1s} signal ($E_b = 285.0$ eV) from the pump oil contaminant. The work function of the spectrometer was taken as 4.0 eV.

Calculations

CNDO(2) and INDO molecular orbital programs were taken from Pople and Beveridge's book.[10] The *ab initio* calculations were completed using QCPE104, "McLyosh Linear Molecule Program I," written by McLean and Yoshimine. Modified CNDO(1) calculations were completed as described previously.[11] In the extended Hückel calculations, coulomb integrals, H_{ii}, were approximated by valence-state ionization potentials.[12] The off-diagonal elements were assigned as

$$H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$$

where S_{ij} is the overlap integral between the ith and jth atomic orbitals. Simple iterative extended Hückel molecular orbital calculations were carried out by performing a Mulliken population analysis on each cycle and correcting the valence-state ionization potentials for net atomic charge q_i

$$H_{ii} = H_{ii}^\circ - (2.0 \text{ eV/charge})q_i$$

The Slater atomic orbital exponents were taken as neutral atom orbital values, μ_i°, corrected for charge.

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Table I

XPS Valence Region Peak Positions for a Solid Sample of NaCN and (−) Eigenvalues Calculated for the Cyanide Ion by Various Molecular Orbital Methods[a]

E_b	Assignment	*Ab initio*	INDO	CNDO (2)	CNDO (1)	Iterative extended Hückel	Extended Hückel
30.52	Na_{2p}						
24.67	1σ	24.73	27.63	25.80	24.62	25.57	30.39
16.98	K^+ impurity (?)						
12.76	2σ	8.25	6.05	7.67	11.27	15.78	18.22
8.96	π	4.75	5.12	5.13	6.32	12.84	15.53
5.28	3σ	4.40	−0.47[b]	1.29	4.54	11.10	12.64

[a] All energies are in eV; the E_b are referenced to the Fermi level. [b] This level is calculated to be slightly antibonding.

$$\mu_i = \mu_i^\circ + 0.35q_i/n^*$$

Here n^* is the effective principal quantum number. In the iterative extended Hückel calculations the off-diagonal Hamiltonian elements were assigned by Cusach's approximation.[13]

Results and Discussion

Cyanide.—An X-ray photoelectron spectrum of a solid sample of NaCN was run in the region of 0–40 eV (binding energy). Figure 1 shows a reproduction of this spectrum, which is a sum of multiple runs. The peaks in the spectrum correspond to the photoionization of electrons from the various valence (*i.e.*, low binding energy) levels in the sample. The strongest peak at 30.52 eV is readily assignable to the photoionization of 2p electrons from the Na^+ ion. This was confirmed by running the spectrum of KCN. The nonsodium peaks in the NaCN spectrum are probably mainly due to photoionization from the cyanide ion. In order to check this we performed a series of molecular orbital calculations on the cyanide ion. The goal was to see if the peaks seen in the NaCN spectrum could be assigned to the different cyanide levels.

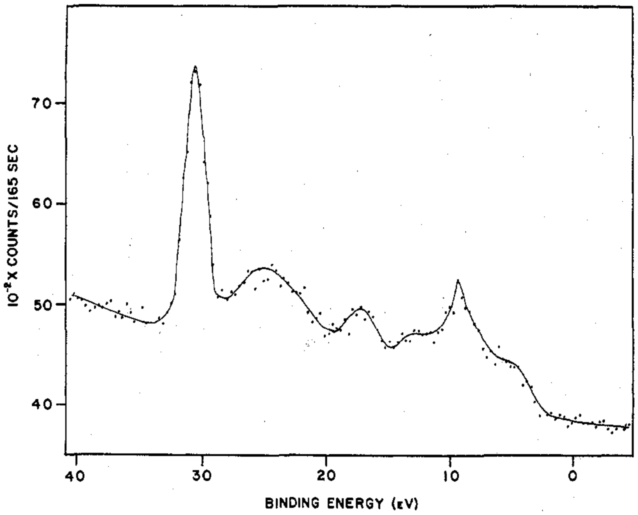

Figure 1.—XPS spectrum of NaCN(s) in the low electron binding energy region.

Many different types of molecular orbital calculations were carried out for the cyanide ion. The results of these calculations are given in Table I. The ordering of the cyanide molecular orbitals can be seen to be the same for all of the calculations. The *ab initio* MO calculation should give us the best determination of the absolute values of the cyanide one-electron eigenvalues. In this calculation a "double ζ plus polarization basis" was used,[14] where the polarization consisted of one 3d σ and one 3d π function for the carbon and nitrogen with orbital exponents of 1.70, 1.80, 1.90, and 2.00, respectively. The carbon–nitrogen bond distance was taken as 1.13 Å. We obtained $E_{el} = -111.9986$ au and $E_{tot} = -92.3209$ au for the cyanide ion. These are considerably better energies than were obtained in the SCF minimal basis set cyanide calculation of Bonaccorsi, *et al.*[15] They reported $E_{el} = -111.1934$ au and $E_{tot} = -91.9273$ au.

The agreement between our *ab initio* eigenvalues and those of the INDO, CNDO(2), and CNDO(1) calculations is moderate (see Table I). The highest filled level in both the INDO and CNDO(2) cases is calculated to be at appreciably higher energy than that for the corresponding *ab initio* level. The agreement between the *ab initio* and extended Hückel treatments is poor, especially for the higher energy levels.

Koopmans' theorem[16] states that the ionization potential for an electron in a particular level is equal to minus the eigenvalue obtained for that level in a Hartree–Fock SCF calculation. The cyanide XPS spectrum can be assigned on this basis (see Table I). In all of the MO calculations there are three molecular orbitals grouped together at lower binding energy and one orbital at much greater binding energy. In the cyanide XPS spectrum (Figure 1) there is a group of three peaks at low binding energy; these peaks have been assigned as corresponding to photoionizations from the three cyanide lowest binding energy filled molecular orbitals (*i.e.*, 2σ, π, and 3σ). In Table I the three peaks have been assigned to specific cyanide molecular orbitals. We realize that since Koopmans' theorem is only approximate, it is quite possible that the three peaks do not fall in exactly the same order as the calculated cyanide eigenvalues. In fact, electron correlation effects might be quite different in magnitude for a σ level as opposed to a π level.

Photoionization from the cyanide 1σ level is probably seen in the broad 24.67 eV peak. The peak observed at 16.98 eV binding energy is difficult to assign. It is defininitely not the $K\alpha_{3,4}$ satellite of the Na_{2p} peak at 30.52 eV. Potassium cyanide has a K_{3p} peak at 17.0 eV and it is possible that the 16.98 eV NaCN peak is due to potassium impurity. However, if the relative peak areas reflect the amount of KCN im-

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purity present, the KCN spectrum that we ran indicates that we would require ~30% KCN impurity. By analysis our NaCN contained at most 5% KCN.

In Table II we give the cyanide eigenvectors as obtained from the *ab initio* calculation. The 1σ molecular orbital is seen to have a fairly large contribution from carbon and nitrogen 1s orbitals. The photoionization cross section for the 1σ level is enhanced by such admixture, and thus it is seen (Figure 1) that the area for the peak assigned to this level is large in respect to the other cyanide peaks. The carbon and nitrogen 1s contributions to the cyanide 2σ molecular orbital are not as large as in the 1σ case. In the group of three low-energy peaks in the cyanide spectrum one peak (4.75 eV) appears to have more area than the other two. It is tempting to assign this peak to photoionization from the 2σ cyanide molecular orbital, because it has the second greatest 1s and 2s character. It must be remembered, however, that although the π cyanide level has perhaps the lowest "intrinsic" cross section, it does have twice as many electrons as either of the other two candidates.

TABLE II

EIGENVALUES AND VECTORS FROM THE *Ab Initio* CYANIDE MO CALCULATION[a]

		Eigenvalue			
	Exponent	1σ	2σ	π	3σ
Orbital		−24.73	−8.25	−4.75	−4.40
C 1s	5.231	−0.1793	0.1566		−0.0743
C 1s	7.969	0.0103	−0.0077		−0.0061
C 2s	1.168	0.0038	−0.2100		0.5523
C 2s	1.820	0.3156	−0.3876		0.2478
C 2pσ	1.256	0.1141	0.0145		−0.4150
C 2pσ	2.726	0.1298	−0.0196		−0.2116
C 3dσ	1.700	0.0495	−0.0288		−0.0215
N 1s	6.119	−0.2382	−0.1213		0.0195
N 1s	8.938	0.0173	−0.0011		−0.0048
N 2s	1.393	0.1323	0.4583		0.0719
N 2s	2.222	0.5303	0.3395		−0.0518
N 2pσ	1.506	−0.1731	0.4242		0.3834
N 2pσ	3.267	−0.0984	0.1832		0.1325
N 3dσ	1.900	0.0562	−0.0218		−0.0392
C 2pπ	1.220			0.3940	
C 2pπ	2.726			0.1471	
C 3dπ	1.800			0.0561	
N 2pπ	1.506			0.5175	
N 2pπ	3.267			0.1836	
N 3dπ	2.000			−0.0421	

[a] Eigenvalues are given in eV; the eigenvectors are not normalized.

There are two general comments that have to be made about the above assignments. First, in comparing the measured binding energies E_b with the calculated eigenvalues it must be remembered that the E_b energies are referenced to the Fermi level, whereas the calculated eigenvalues are referenced to the vacuum level. Agreement in the absolute values of the two numbers cannot be expected. It is somewhat remarkable that many of the values do seem to agree so closely. This must be the result of a balance of work function potentials, crystal lattice potentials, etc. The second general comment is that the assignments of XPS peaks based on MO calculations alone are not conclusive. As has been pointed out in reference 9 there are no formal selection rules in XPS. For instance, satellite peaks attributed to shake-up[8] processes are seen; in this case an electron is photoionized simultaneous to excitation of a second electron. Nevertheless, even with these two reservations it does seem possible to assign many XPS spectra using MO calculations.[8,9]

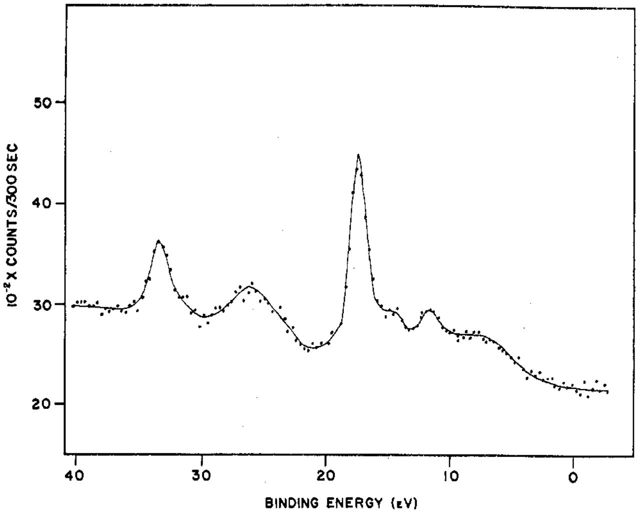

Figure 2.—XPS spectrum of KNO_3(s) in the low electron binding energy region.

Nitrate.—XPS data were collected for a sample of potassium nitrate and are presented in Figure 2 and Table III. The strong peaks at 33.40 and 17.37 eV are probably dominantly the K_{3s} and K_{3p} peaks. Any nitrate peaks in these regions are obscured by these two strong potassium peaks. Unfortunately, data were only collected for the potassium salt.

TABLE III

XPS VALENCE REGION PEAK POSITIONS FOR A SOLID SAMPLE OF KNO_3 AND (−) EIGENVALUES CALCULATED FOR THE NITRATE ION BY VARIOUS MOLECULAR ORBITAL METHODS[a]

E_0	Assignment	INDO	CNDO(2)	CNDO(1)	Extended Hückel
33.40	K_{3s}				
	$1a_1$	43.24	41.64	36.88	41.54
26.27	$1e'$	31.84	30.92	29.79	35.92
17.37	K_{3p}				
	$2a_1'$	15.98	16.04	18.79	22.52
14.59	a_2''	14.61	16.01	13.94	20.11
11.56	$2e'$	12.56	13.83	13.91	19.91
7.46[b]	a_2'	5.42	6.24	8.64	17.83
	e''	4.90	5.48	8.11	18.37
	$3e'$	4.89	5.29	7.69	18.07

[a] All energies are in eV, and E_b are referenced to the Fermi level. [b] Broad peak.

Molecular orbital calculations were carried out for the nitrate ion using different MO methods. The results (see Table II) show that the nitrate ion has eight filled molecular orbitals and that approximately the same molecular orbital ordering is found by the various MO methods. Only in the case of the three lowest binding energy orbitals is there variance, the extended Hückel method giving an order slightly different from that of the INDO and CNDO calculations. The XPS peaks have been tentatively assigned to the various filled molecular orbitals in Table III. The peak at 7.46 eV is seen to be very broad; this could reflect the fact that the nitrate ion apparently has three closely spaced low binding energy levels. A nitrate molecular orbital level is calculated to be in proximity to the K_{3s} peak, and another near the K_{3p} peak. It would be very desirable to have further runs on other salts of the nitrate ion.

In summary, there is a moderate correlation between the calculated MO levels and XPS peaks for the nitrate ion. This was also found to be true in the case of the cyanide ion. In both anions the CNDO(1) method gives the best overall agreement with the experimental XPS energies. However, this could very well be fortuitous. In the case of the cyanide MO calculations, the CNDO calculations come the closest to the *ab initio* calculation, with the INDO calculation seemingly having trouble with the lowest binding energy levels. Both of the cyanide extended Hückel treatments give poor agreement with the *ab initio* calculation. The same qualitative trends are also evident in the nitrate ion MO calculations.

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CONTRIBUTION FROM THE DÉPARTEMENT DE CHIMIE,
UNIVERSITÉ DE MONTRÉAL, MONTRÉAL 101, QUEBEC, CANADA

Calorimetric Studies in the Halide–Hydrogen Chloride Systems

BY R. L. BENOIT,* M. RINFRET, AND R. DOMAIN

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The free energy and enthalpy of the reactions $X^-(solv) + HCl(solv) = HClX^-(solv)$ were determined at 30° from calorimetric measurements in sulfolane, a very weakly basic dipolar aprotic solvent. $X^-(solv)$ denotes solvated chloride, bromide, and iodide ions. From the heat of solution of gaseous hydrogen chloride, the following enthalpy changes are obtained for the reactions $X^-(solv) + HCl(g) = HClX^-(solv)$: 13.9, 10.7, and 8 kcal mol^{-1}, respectively, for Cl^-, Br^-, and I^-. These enthalpies which are minimum values for hydrogen bond energies for $HClX^-$ are compared with values previously predicted from reported measurements on some solid halide salts–hydrogen chloride systems.

Introduction

Hydrogen dihalide HX_2^- anions[1] are well characterized in salts whose lattice is stabilized by large cations such as tetraalkylammonium. The mixed HXY^- anions have received less attention. Attempts have been made to evaluate the corresponding hydrogen bond energies. In aqueous solutions, HF_2^- is well-known but there is no evidence for the other ions which are apparently too unstable. However, in some nonaqueous solvents, the equilibria

$$X^-(solv) + HY(solv) = HYX^-(solv) \qquad (1)$$

have been studied for HCl_2^- and HBr_2^-.[2,3] Dipolar aprotic solvents, in particular, favor the formation of hydrogen dihalide ions because the differences in solvation energies for small (X^-) and large (HYX^-) anions[4] are considerably smaller in these solvents than in protic solvents.

Among the dipolar aprotic solvents, sulfolane was selected for a study of reactions 1 (X = Cl, Br, I; Y = Cl) as it behaves as a very weak base[5] so that HCl does not appreciably dissociate, its dissociation constant is estimated to be $\sim 10^{-13}$. Results of a preliminary nmr study were recently published.[6] The present calorimetric investigation was carried out to provide thermodynamic data for the reactions involving the formation of HCl_2^-, $HClBr^-$, and $HClI^-$ ions. Such data are combined with the heat of solution of HCl in sulfolane to lead to values which are related to hydrogen bond energies and can be compared with previous estimates.

Experimental Section

Materials.—Sulfolane was purified according to a procedure described previously.[4] Tetraethylammonium chloride and bromide and tetrabutylammonium iodide were Eastman Kodak White Label products. Both compounds were recrystallized from ethanol and dried under vacuum at 40°. Solutions of the halide salts were prepared by weighing. Concentrated solutions of hydrogen chloride were obtained by saturation with Matheson anhydrous HCl gas after passage through a Dry Ice–acetone trap. The HCl concentration was determined by titration with standardized NaOH after flooding of the sample with water.

Apparatus and Procedure.—Heats of reaction were measured with an LKB-Produkter AB (Stockholm, Sweden) Model 8725-2 Isoperibol calorimeter. It consists of a 25-ml Pyrex reaction vessel equipped with a 1700 ohm thermistor, a 50 ohm heater, and a sample-holder stirrer. Sealed 1-ml glass ampoules filled with a 3 *M* HCl solution were attached to the holder. The reaction vessel containing the halide solution is enclosed in a chrome-plated submarine jacket, which, in turn, is kept in a thermoregulated bath maintained at 30.016 ± 0.001°. The calorimeter is calibrated electrically before and after each run by means of a Hewlett-Packard 740B standard calibrator. The current pulse into the heater is predetermined by a HP 5214L preset electronic timer followed by a flip-flop circuit driving a high-speed miniature Clare mercury wetted relay with a response time less than 1 msec.

The thermistor temperature sensor is connected in series with a Guildline 9801T temperature controlled four-terminal resistor (calibrated to 1 ppm) and a Keithley 225 constant-current source (set at 200 μA). The voltage drops at the thermistor and the four-terminal resistor are compared with a Guildline 9810L isolating potential comparator.[7] The difference signal between the thermistor and the resistance settings, in increments of 10 ohms (0.125°K), is recorded on a strip chart recorder, yielding a complete time–resistance curve.

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