Studies of the Bonding in Acetonitrile Adducts[1]

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Abstract: The results of force constant determinations and molecular orbital calculations for the 1:1 adducts of acetonitrile with the Lewis acids ICl, $SnCl_4$, and BF_3 are reported. It is found that the C≡N frequency increases only slightly as a result of kinematic coupling in the subsystem C≡N→acid. However, the C≡N force constant is shown to increase significantly upon coordination of acetonitrile and is the main cause for the frequency increase. The molecular orbital calculations support this and allow us to conclude that the N_{2s} orbital, in overlapping the C_{2s} and $C_{2p\sigma}$ orbitals, is responsible for the observed strengthening of the C≡N link upon coordination of CH_3CN to Lewis acids.

A phenomenon which has long been of interest and use to the coordination or acid–base chemist is the alteration of donor (and acceptor) vibrational frequencies upon formation of the "coordinate bond." In addition to the structural applications of these shifts, qualitative, and in selected instances quantitative, estimates of interaction strengths have been determined from the magnitudes of the frequency shifts of normal vibrations involving the donor (or acceptor) atom.

A few acids, those in which the acceptor site is a hydrogen atom, would seem to allow a quantitative and linear relationship between hydrogen stretching frequency shift and enthalpy of adduct formation or base strength.[2] This may be attributed, in part, to the small mass of the hydrogen atom. There also appears to be a linear relationship between the energy of the H···B bond and the change in dissociation energy of the O–H bond.[3]

A molecular parameter more meaningful than frequency shift as a criterion of the strength of a coordinate bond is the force constant for stretching of that bond. An alternative is to study the change in force constant of a bond adjacent to the coordinate bond. In the case of a donor frequency shift, this potential constant is anticipated to be sensitive to the acidity of the acid and the nature of the bond which it forms with the donor. A rough estimate of this sensitivity is indicated by the magnitude of the frequency change upon coordination, as noted above.

It is the purpose of this paper to examine the changes in vibrational frequency and force constant of the CN link in CH_3CN upon coordination to various acids. Acetonitrile is desirable as a reference donor because of the symmetry of its adducts,[4] the energy of the "CN vibration" (in a region uncomplicated by the presence of other absorption bands), and the small number of atoms, all of which facilitate a force constant calculation. Indeed, this molecule has been the subject of normal coordinate analyses; Urey–Bradley,[5] simple valence force field,[6] and the hybrid orbital force field approximations[7] have been applied.

A most interesting property of acetonitrile, which is true of other –CN and –NC donors, is the *increase* in magnitude of the "CN stretching frequency" upon adduct formation by the N (or C in the case of RNC) lone pair of electrons. One factor which might be expected to make an important contribution to this frequency increase is the kinematic coupling of the CN and N–acid bonds during excitation of the CN normal mode.[8] In addition, a mechanism has been proposed[9] for the frequency increase which can be classified according to Bent's hybridization arguments,[10] while yet another argument is based on "electron" repulsions.[11] These latter two mechanisms imply an increase in the C–N stretching force constant upon coordination.

In order to ascertain the validity of these predictions, we have examined the potential constants for the adducts and their compatibility with these mechanisms. While rigorously quantitative descriptions are not possible, sufficient accuracy is possible to determine the cause of the frequency increase and its origin in terms of a molecular orbital treatment.

Experimental Section

$CH_3CN\cdot BF_3$. The adduct was prepared by reaction of Baker Analyzed Reagent CH_3CN and Matheson BF_3.[4] The adduct was sublimed under reduced pressure in a closed system prior to use.

$SnCl_4\cdot CH_3CN$. This was prepared *in situ* in benzene[8] (which had been dried over Linde 4-A sieves) by reacting a slight excess of $SnCl_4$ (Fisher Certified Reagent) with CH_3CN which had been purified by 4-A sieves.

Infrared Spectra. Spectra of the boron trifluoride adduct were obtained from KBr pellets, Nujol, and Fluorolube mulls, and methylene chloride solution. The tin adduct spectrum was obtained from the benzene solutions. All operations were performed in a drybox and the samples protected from atmospheric moisture during the recording of the spectra. All spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer.

Calculations

A. Normal Coordinate Analyses. The normal coordinate analyses were performed on the University of Illinois IBM 1401/7094 installation.[12] The basic program was obtained from Dr. J. H. Schachtschneider;

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[1] Abstracted in part from the Ph.D. thesis of K. F. Purcell, University of Illinois, Urbana, Ill., 1965.

[2] M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

[3] K. F. Purcell, Ph.D. Thesis, University of Illinois, 1965.

[4] J. L. Hoard, T. B. Owen, Z. Buzzell, and O. N. Salmon, *Acta Cryst.*, 3, 121 (1950).

[5] I. Nagakawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 513 (1962).

[6] K. Venkateswarhu and R. Thanalkshmir, *Indian. J. Pure Appl. Phys.*, **1**, 64 (1963).

[7] J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964).

[8] T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 4175 (1961).

[9] H. A. Brune and W. Zeil, *Z. Naturforsch.*, **16a**, 1251 (1961).

[10] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[11] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 2293 (1964).

[12] Partially supported by the National Science Foundation (Grant NSFGP700).

Table I. Vibrational Frequencies for A_1 Vibrations of Acetonitrile and Some Adducts (cm^{-1})

	CH_3CN	$CH_3CN \cdot ICl$[a]	$CH_3CN \cdot SnCl_4$	$(CH_3CN)AlCl_3$[b]	$(CH_3CN)_4Zn$[c]	$CH_3CN \cdot BF_3$
$\bar{\nu}_{CH_3}$	2954	2954	2954	2934	2941	2935
$\bar{\nu}_{CN}$	2266	2278	2302	2330	2306	2355
δ_{CH_3}	1371	1371	1351	1363	1368	1362
$\bar{\nu}_{CC}$	920	920	940	957	939	965

[a] E. Augdahl and P. Klaboe, *Spectrochim. Acta*, **19**, 1665 (1963). [b] A. Terenin, B. Filimonov, and D. Bystrow, *Z. Elektrochem.*, **62**, 180 (1958). [c] See ref 22.

Table II. Symmetry Force Constants for CH_3CN and CD_3CN

	CH_3CN alone	$CH_3CN + CD_3CN$		Variation of $F_{CC,def}$[a] CH_3CN	CH_3CN	CH_3CN
F_{CH_3}, mdynes/Å	5.014	5.016	5.019	5.021	5.022	5.024
F_{CN}, mdynes/Å	17.077	17.366	17.705	17.619	17.680	17.696
F_{def}, mdynes Å	0.486	0.490	0.587	0.565	0.586	0.604
F_{CC}, mdynes/Å	6.347	5.746	5.388	5.399	5.288	5.257
$F_{CC,def}$, mdynes	...	...	−0.357	−0.257[a]	−0.357[a]	−0.457[a]
$\lvert A \rvert / \pi A_{ii}$[b]	0.4	0.7	0.6	0.8	0.9	0.9
Av error in frequencies, cm^{-1}	0.0	25	2.5	0.0	0.0	0.0

[a] The F_{CC} deformation interaction constant was held fixed in each of the three calculations. [b] $A = Z'J'WJZ$.

the calculational method has been described by several authors in addition to Schachtschneider.[13-15] In essence, the G matrix elements were machine computed and spot checked with Wilson's formulas.[16]

The G matrix, for symmetry or internal coordinates, is accompanied by observed eigenvalues and trial force constants as input to a force constant refinement program. All force constants are simultaneously refined and various output data follow each refinement step so that the course of the calculation may be followed. The final output consists of the refined potential constants, the calculated frequencies and their agreement with the observed eigenvalues, the potential energy distribution, the eigenvectors, the coefficients of the normal equations, and various statistical entities.

B. Molecular Orbital Calculations. These calculations were performed with an "extended Hückel theory" program which originated with Hoffmann.[17] This program has been modified to allow iterative charge adjustment of Slater exponents and valence-state ionization energies until a self-consistent set of atom charges is obtained.[18] Output consists of charge-adjusted Slater exponents, charge-adjusted valence-state ionization energies, atom charges, overlap integrals, molecular orbital energies and total energy, eigenvectors, Mulliken overlap populations in various forms, charge matrix, and orbital charges.

Results

Vibrational Analyses. The vibrational frequencies and assignments of acetonitrile and its adducts with ICl, Zn^{2+}, $SnCl_4$, $AlCl_3$, and BF_3 are set out in Table I. The molecular parameters for CH_3CN and $CH_3CN \cdot BF_3$ were obtained from the literature.[4,19]

Analysis of Acetonitrile. The force constants of acetonitrile were computed only for the A_1 symmetry coordinates as our interest lies in the force constants for CN and CC stretching vibrations. The calculations were performed for CH_3CN alone, CD_3CN alone, and then for the two together. A perfect fit of frequencies with rapid convergence resulted in the case of CH_3CN alone. Here a diagonal F matrix was assumed as a result of the limited number of frequencies.

The attempts at calculation of a diagonal F matrix for CD_3CN were characterized by very seriously ill-conditioned[14] sets of normal equations. Use of the final constants for CH_3CN alone as a starting point for CD_3CN resulted in failure of the refinement process. Serious ill-condition of the equations and poor frequency fits were found for the simultaneous refinement of CH_3CN and CD_3CN. Owing to the existence of a large interaction force constant between the symmetric methyl deformation and C–X stretch in CH_3X compounds,[14] it was decided to include this constant for refinement in the simultaneous calculations of CH_3CN and CD_3CN. This solved the difficulty as rapid convergence accompanied by well-conditioned equations resulted. The results of these calculations are presented in Table II.

In order to obtain some measure of the effect of kinematic coupling of the N→acid coordinate with the CN coordinate in the adducts and to estimate the effect of the mass of the acid on the "CN stretching frequency," the following calculations were performed. The vibrational frequencies of the hypothetical molecule $CH_3CN \rightarrow$atom were calculated by holding the set of force constants obtained for CH_3CN fixed and by varying both the force constant of the N→atom bond, and simultaneously, the mass of the atom. The results, $\bar{\nu}_{CN}$ *vs.* atom mass for each assumed value of the N→atom force constant, are given in Figure 1. In

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(13) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85, 117 (1963).

(14) J. Aldous and I. M. Mills, *ibid.*, **19**, 1567 (1963).

(15) J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 1289, 1296, 1720 (1960).

(16) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 303.

(17) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); (b) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(18) For details see P. C. Van Der Voorn and R. S. Drago, to be published.

(19) "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publication No. 11, The Chemical Society, London, 1958.

Table III. Symmetry Force Constants for CH_3CN Using Adduct Frequencies

	ICl	$SnCl_4$	Zn^{2+}	$AlCl_3$	BF_3
F_{CH_3}, mdynes/Å	5.022	5.022	4.977	4.952	4.955
F_{CN}, mdynes/Å	17.896	18.225	18.287	18.611	19.022
F_{def}, mdynes Å	0.586	0.567	0.581	0.575	0.573
F_{CC}, mdynes/Å	5.279	5.549	5.529	5.779	5.882
$F_{CC,def}$,[a] mdyne	−0.357	−0.357	−0.357	−0.357	−0.357
$\lvert A\rvert/\pi A_{ii}$	0.9	0.8	0.9	0.8	0.9
Av error in frequencies, cm^{-1}	0.0	0.0	0.0	0.0	0.0

[a] The $F_{CC,def}$ interaction constant was held fixed at the value found for CH_3CN. The insensitivity of F_{CN} to slight changes in this interaction constant was shown in Table II.

Figure 2 we have shown the relationship between $\tilde{\nu}_{CN}$ and force constant for the two atom masses 11.0 and 261.0.

Calculations of CH_3CN force constants, with the C–C stretch–CH_3 deformation interaction constant fixed at −0.357, were performed using the four A_1 frequencies observed in each of the adducts. Here we are making an opposite approximation to the one above. The changes in CH_3CN frequencies are considered to be due entirely to electron redistribution within CH_3CN. Convergent force constants were found for all adducts; each was accompanied by well-conditioned normal equations and a perfect fit of eigenvalues. The results are given in Table III.

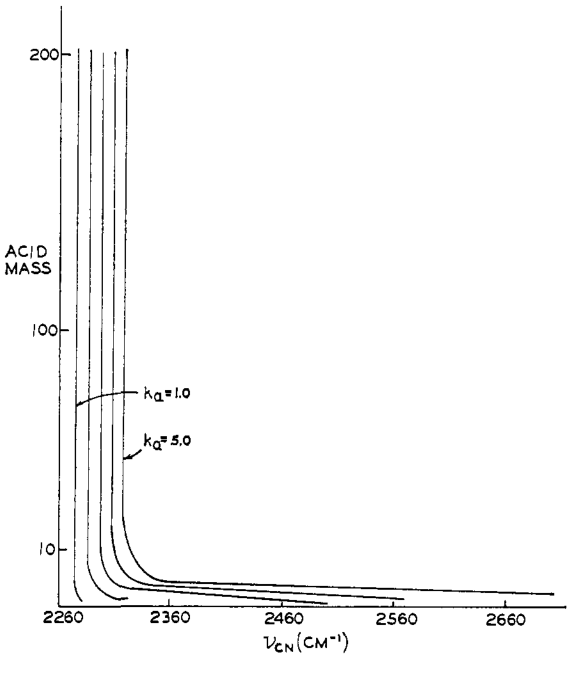

Figure 1. $\tilde{\nu}_{CN}$ as a function of adduct bond force constant and acid mass.

One further approximation was made in an effort to estimate an upper limit to the N–acid force constant in the Zn^{2+}, $SnCl_4$, and BF_3 adducts. Again, the model was $CH_3CN \rightarrow$ atom, and the CC stretching and CC, methyl deformation interaction force constants were held fixed while the other four constants (CH, CN, CH_{def}, and N–atom) were adjusted for the four adduct frequencies. The results are presented in Table IV.

Table IV. Force Constants of L·Acid

	Zn^{2+}	Zn^{2+}	$SnCl_4$	BF_3
F_{CH_3}, mdynes/Å	4.978	4.978	5.022	4.958
F_{CN} mdynes/Å	18.258	18.234	18.166	18.906
F_{def}, mdyne Å	0.582	0.583	0.569	0.578
F_{CC}, mdynes/Å	5.398	5.288[a]	5.288[a]	5.288[a]
$F_{CC,def}$,[a] mdyne	−0.357	−0.357	−0.357	−0.357
F_{NA}, mdynes/Å	0.49[b]	0.886	0.968	2.027
$\tilde{\nu}_{NA}$, cm^{-1}	179	239	210	348
$\lvert A\rvert/\pi A_{ii}$	0.9	0.8	0.8	0.8
Av error in frequencies, cm^{-1}	0.0	0.0	0.0	0.0

[a] The force constant was held fixed at the value found for CH_3CN.
[b] This force constant was held fixed at the value reported in ref 22.

Discussion

The fact that no interaction constant was required for CH_3CN to obtain a good fit between calculated and observed frequencies is interesting and illustrates a point which is frequently overlooked. This means that the diagonal force constants could be adjusted to account for the absence of the interaction constant in CH_3CN and would suggest that the nature of the normal modes of CH_3CN are greatly different from those of CD_3CN. That this is so has been shown in detail by Fletcher, *et al.*[20] The effect on the CN, CC, and CH_3 deforma-

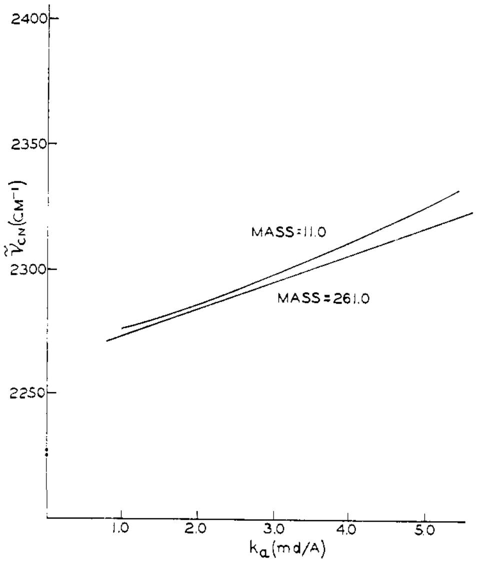

Figure 2. ν_{CN} as a function of adduct bond force constant for acid masses of 11.0 and 261.0.

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(20) W. H. Fletcher, C. S. Shoup, and W. T. Thompson, *Spectrochim. Acta*, **20**, 1065 (1964).

tion force constants (Table II) is significant and shows that while a certain interaction constant may be assumed to be zero in an analysis and good results follow therefrom, in no way does this establish that the constant has a value of zero. Moreover, determination of the value of such a constant by the inclusion of more data (Coriolis coupling constants, isotopic frequencies) may significantly alter the values of the other constants. One must be cautious in comparing force constants calculated using different approximations. In this work, the calculations were performed with and without the C–C, methyl deformation interaction constant, and the nature of our conclusions is the same in both. We report on only the calculations which include this constant. The agreement of our values in Table II with those of Duncan[7] is gratifying.

From the results of the calculation of mass and force constant (adduct bond) effect on $\bar{\nu}_{CN}$, it is immediately apparent that atom masses of ten or greater for the acid all have the same effect on the CN stretching frequency. In addition, the adduct force constant can*not* be used to explain *all* of the increase in CN stretching frequency. The force constants for the adduct bonds are expected to lie below 2.5 mdynes/Å (*vide infra*) and should parallel the CN frequency. This means that kinematic coupling could account only for approximately 10 cm^{-1} in the adduct with Zn^{2+} and approximately 50 cm^{-1} in the BF$_3$ complex.

In adducts with oxo donors a decrease in stretching frequency of the oxo bond is actually observed; the coupling effect, whatever its magnitude there, is overshadowed by changes in the oxo bond strength. It is customary to ascribe the decrease in frequency to the polarization of the oxo bond by the acid.[21] Polarization effects must be of secondary importance in nitriles, for an increase in the CN force constant is clearly required. While, on the one hand, it is not possible to account for the change solely on the basis of kinematic arguments, it is possible to account for the frequency increase by increases in the CN and CC force constants (note that $\bar{\nu}_{CC}$ also slightly increases). Again, the force constants of these calculations are not quite the true values that would be obtained from a complete treatment of each adduct. However, the increases are significant and physically acceptable solutions are achieved when the adduct bond is ignored. It is encouraging that the potential energy distributions in the adducts were not found to differ significantly from that in the free ligand. This implies that the approximation of relatively weak force constants for the adduct bonds does not force an increase in CC and CN coupling to explain frequency shifts even in the BF$_3$ adduct. If the adduct bond force constant were of significance, a poor fit of the CH$_3$ deformation, CC, and CN stretching frequencies and/or a change in the coupling of these vibrations might be expected.

The results in Table IV are interesting in that they set an approximate upper limit on the adduct bond force constant. Evans and Lo[22] have performed an analysis on CH$_3$CN·Zn^{2+} using the Urey-Bradley approximation. There, they obtained a N–Zn^{2+} constant of 0.49 mdyne/Å. In our approximation in Table IV (first entry) we have constrained this value (as well as the interaction constant) and refined the other constants. The final values of these constants are not greatly different from those in which the C–C constant was fixed at its value in CH$_3$CN except for the adduct bond, and the value in the latter instance is about 0.4 mdyne/Å. too high. Similarly, the adduct bond constants for SnCl$_4$ and BF$_3$ are most likely overestimated.

The true situation with respect to the CC stretching force constant is such that the true value in each adduct lies somewhere between the values in Table IV and the corresponding values in Table III. The effect of underestimating the C–C force constant on the adduct bond force constant is to make the latter too large. For a true C–C value in each case larger than that of uncomplexed CH$_3$CN, the calculated adduct bond constant would be lower.

The calculated adduct bond frequencies are also given in Table IV. The absorption bands in the complexes which have been assigned to these coordinates are (cm^{-1}): Zn (180), SnCl$_4$ (320), and BF$_3$ (630). The calculated frequencies for the SnCl$_4$ and BF$_3$ adducts are appreciably lower than these values. In the case of the SnCl$_4$ complex, inclusion of Sn–Cl vibrations in the analysis would most certainly improve this apparent disparity. Three of the Sn–Cl vibrations have been assigned[23] at 365, 339, and 306 cm^{-1}. The adduct vibration should then be coupled rather strongly with these vibrations and result in an increase in the frequency assigned to the adduct bond stretch. A similar situation with the BF$_3$ adduct is expected to exist. Taylor[24] has found a great deal of mixing of the B–F vibrations with the adduct bond stretch in NH$_3$·BF$_3$. Further support for the approximate correctness of these force constants comes from the application of chemical intuition to the fact that Taylor[24] found the N–B force constant in NH$_3$·BF$_3$ to be 4.0 mdynes/Å.

A literature report[8] on the results of very approximate calculations on nitrile–SnCl$_4$ adducts appears to have led to an overestimation of the N→Sn force constant. Our attempts to repeat the same hand calculation led to a N→Sn force constant of much smaller magnitude (0.5 mdyne/Å) and a larger CN constant (18.1 mdynes/Å) than those reported there. This and the results of the more detailed analyses in this work seem to indicate that the earlier calculation is in error (Table IV and Figure 2), and arguments that kinematic coupling is most important should be revised.

The results of Tables III and IV may be used to predict the order of acidity for these acids *in their complexes* with acetonitrile. This order, both from F_{CN} and F_{NA}, is ICl < SnCl$_4$ ~ Zn^{2+} < AlCl$_3$ < BF$_3$.

As a result of these investigations, it is safe to say that the nitrile frequency increase observed upon coordination is due to the fact that *the force constant for the CN bond in CH$_3$CN, and presumably all nitriles and isonitriles, increases upon coordination.* The coupling of the adduct bond with the CN bond causes only a minor increase of the CN stretching frequency.

Calculations of CN Bond Strength in CH$_3$CN and CH$_3$CNBF$_3$. As noted in the introductory section,

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[21] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[22] J. C. Evans and Y.-S. Lo, to be published.

[23] I. R. Beattie, G. P. McQuellan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

[24] R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 59.

there have been two mechanisms proposed to explain the increase in the nitrile force constant. One of those involves an increase in CN bond dissociation energy (force constant) due to rehydridization at the nitrogen. In doubly bonded donor atoms, coordination at the more electronegative atom weakens the multiple bond, and this has been explained[8,21] by polarization of the π bonds which appears to result from an increase in the electronegativity of the donor atom. Other alterations in the character of the multiple bond either parallel the changes in π orbitals with respect to the effect on the force constant or, if opposing, are of secondary importance. Such does not appear to be the case in nitrile coordination since the CN bond distance decreases while the force constant increases. These facts suggest the link is more stable after coordination than before, and any destabilization of the π orbitals must be offset by stabilization of the σ molecular orbitals. With regard to assessing these changes, there are many factors which contribute to the energies of the bonds in systems such as these, and it is difficult and dangerous to single out any one factor such as overlap integrals, energy matching of AO's, etc., as being responsible for changes in the molecular orbitals upon coordination.

Certainly the most reliable criterion of bond strength in calculations such as these is the energy(ies) of the molecular orbitals defining that bond. (Choice of the proportionality constant in the Wolfsberg-Helmholz equation[25] does not affect our conclusions.) By performing a Mulliken overlap population analysis[26] on each MO, we were able to ascertain the three orbitals $\sigma + 2\pi$ which contributed most to the bonding in the CN group (overlap populations larger by a factor of 2) and, to a first approximation, take these as the "CN" σ and π orbitals. We find by examining the one-electron energies for these three molecular orbitals that these orbitals are definitely stabilized in the adduct relative to the isolated donor, a fact which implies greater stability of the CN link in the adduct.

In order to determine the effect of the N_{2s} orbital on the strength of the CN link, we have returned to the results of the Mulliken overlap population analysis. The use of eigenvectors alone here has somewhat dubious meaning owing to the fact that overlap integrals have not been neglected in the extended molecular orbital calculations. More important, there is no *one* CN σ orbital and, hence, no *one* N_{2s} coefficient. As Mulliken has noted, the energy of a given MO depends on the net atomic populations, the overlap populations, the energies of the AO's, and the overlap energies of the various pairs of AO's. A straight comparison of overlap populations is valid only between combinations of comparable overlap energy (*i.e.*, of equal β_{ij}/S_{ij}). The quantities of interest here, in terms of the Mulliken analysis, are the changes in total overlap populations and overlap energies between the pairs of AO's. We have calculated the overlap energies (β_{ij}) for the C_s–N_s, $C_{p\sigma}$–N_s, C_s–$N_{p\sigma}$, $C_{p\sigma}$–$N_{p\sigma}$ orbitals relative to the average of AO energies, from the 2 × 2 secular determinants for each pair using the charge adjusted overlap integrals and valence-state ionization energies of the extended Hückel treatment. The results are given in Table V. The corresponding overlap populations and overlap integrals are also presented. According to Mulliken's formulations[26] the quantities $\rho_{ij}\beta_{ij}/S_{ij}$ measure the contribution of the bonding electron density (ρ_{ij}) of each AO pair (i,j) to the energy of the molecule. It should be emphasized that the ρ_{ij}'s are the *total* overlap populations, (summed over *all* occupied MO's). The following interpretation is, therefore, not subject to the selection of one σ and two π MO's.

Table V. Overlap Energies, β_{ij}, Overlap Populations, ρ_{ij}, and Overlap Integrals, S_{ij}, for AO Pairs in CH_3CN and $CH_3CN \cdot BF_3$

AO's		β_{ij},			
i	J	ev	ρ_{ij}	S_{ij}	
N_s	C_s	−21.98	0.2646	0.4812	CH_3CN
N_s	C_σ	−17.64	0.1435	0.4803	
N_σ	C_s	−13.68	0.2817	0.4339	
N_σ	C_σ	−5.47	0.1822	0.3057	
N_π	C_π	−5.57	0.4435	0.3093	
N_s	C_s	−22.41	0.3085	0.4806	$CH_3CN \cdot BF_3$
N_s	C_σ	−18.43	0.1800	0.4859	
N_σ	C_s	−13.69	0.2271	0.4268	
N_σ	C_σ	−5.70	0.1559	0.3047	
N_π	C_π	−5.80	0.4267	0.3087	

To correctly assess the cause for stabilization of the CN link, we must find the net change in electron density from the various pairs of AO's weighted by their effect on the energy of the composite link. Table VI displays this information. Here we find that, indeed, the N_{2s} orbital, in overlapping with the C_s and C_σ orbitals in all the σ MO's, is the major cause for stabilization of the CN group following adduct formation. We might note that the use of overlap populations alone would have been somewhat misleading with respect to the π molecular orbitals. In Figure 3 are given the π molecular orbital diagrams for the CN orbitals of CH_3CN as well as those for the adduct $CH_3CN \cdot BF_3$. In keeping with the increased positive charges on C and N in the adduct (increased electronegativity), the C and N atomic orbitals are at slightly lower energies; also, the N orbitals are lowered in energy more than the C orbitals as expected. The interesting fact is that the π MO's in the adduct are lower in energy than are the π orbitals of the donor (both absolutely and relative to the average AO energies). It is just this fact that makes indiscriminate use of overlap populations, in general, erroneous.

Table VI. Change in $\rho_{ij}\beta_{ij}/S_{ij}$ for CH_3CN and $CH_3CN \cdot BF_3$

	C_s	C_σ	C_π
N_s	−2.30	−1.56	. . .
N_σ	+1.60	+0.34	. . .
N_π	. . .	. . .	−0.03

One other aspect of these calculations, the predicted change in "CN" vibrational intensity, is interesting. The marked increase in absorption intensity of the CN vibration upon coordination of the N "lone pair" has been attributed[27] to increased charge separation

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(25) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).
(26) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 1846, 2343 (1955).
(27) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

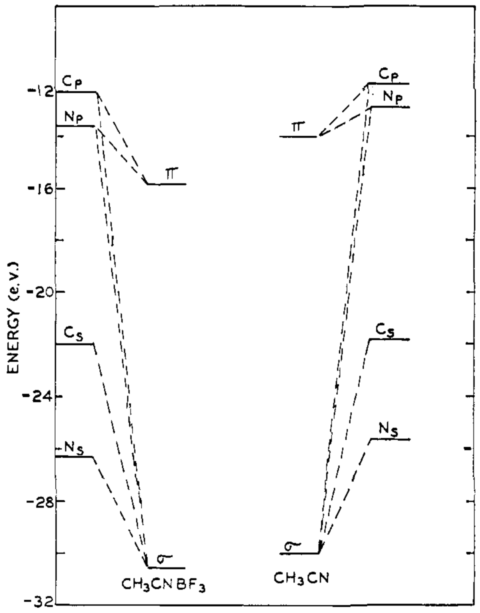

Figure 3. Molecular orbital diagrams for the "CN orbitals" of $CH_3CN \cdot BF_3$ and CH_3CN.

(dipole moment) in the CN link. This rationalization fails to take into account the fact that the *normal mode* referred to as the CN stretching mode actually is different for the adduct and free ligand. The assumption of a greater "CN" dipole is apparently based on charge flow, incurred by coordination, in the CN link. The results of the extended Hückel calculation reported here indicated that the "CN" dipole is smaller in the BF_3 adduct than in CH_3CN. In addition to a slightly shorter bond distance in the adduct, the difference in C and N net charges decreases from slightly greater than 1 in the donor to approximately 0.8 electrostatic unit in the adduct! The vibrational analyses indicate that the cause for the intensity increase may well lie in the fact that the "CN" normal mode changes upon coordination. The eigenvectors for the "CN" normal mode in the adduct show that the NB bond stretching vibration is activated (*cf.* kinematic coupling above) in this normal mode, and the charge on the boron atom, from the molecular orbital calculation, is approximately a full atomic unit. The inclusion of motion of this highly charged atom in the normal mode would cause an increase in the absorption intensity of the normal mode. In keeping with this argument, the intensity of the "NB" stretching vibration at ~600 cm^{-1} is appreciably larger than that of the "CN" vibration, indicating that stretching the "NB" bond will contribute significantly to the intensity of the "CN" vibration.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

Kinetic Study of the Reaction of Peroxydiphosphate with Iodide

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Received September 24, 1965

Abstract: The rate of the reaction of potassium peroxydiphosphate with potassium iodide has been measured in acid media at different reactant concentrations at 25°. The reaction takes place through at least three main paths, which can be represented as

$$H_3P_2O_8^- + I^- \longrightarrow HPO_4^{2-} + H_2PO_4^- + I^+$$
$$H_3P_2O_8^- + H_2O \longrightarrow H_2PO_4^- + H_2PO_5^- + H^+$$
$$H_2P_2O_8^{2-} + I^- \longrightarrow 2HPO_4^{2-} + I^+$$

followed by very fast reactions which give the final products. The first path is the easiest to verify; the existence of the others has been confirmed with runs performed in the absence of iodide and by means of a study of the salt effects, respectively. The differences in behavior toward the iodide ion of the peroxydiphosphate and of the peroxydisulfate ion are discussed.

The peroxydiphosphate ion reacts readily with the iodide ion in acid media to form phosphoric acid and iodine.[1] The kinetics of this reaction, however, has never been investigated quantitatively, as far as we know, so that its mechanism is unknown. This is in contrast with the reaction of peroxydisulfate with iodide, which takes place in neutral media, and which has been extensively investigated.[2,3] The reaction of peroxydiphosphate with iodide in the absence of acid could have escaped attention because iodate is formed, since a solution of $K_4P_2O_8$ is decidedly alkaline.[1] On the other hand, it is possible that the oxidation of the iodide ions take place mainly through the formation of peroxymonophosphate; the latter, in fact,

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