The Photoelectron Spectrum of the Dimethyl Ether–Hydrogen Chloride Complex

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Abstract: The He(I) photoelectron spectrum of the gas-phase heterodimer of $(CH_3)_2O$ and HCl has been measured using a nozzle inlet sampling a high-pressure equilibrium mixture of the two gases. A spectrum stripping procedure allows the derivation of a spectrum corresponding to that of the "pure" complex. Interpretation of the spectrum with the aid of GAUSSIAN 70 molecular orbital calculations indicates that the measured monomer-to-dimer ionization potential shifts are due to an inductive transfer of electron density of about 0.05 e from $(CH_3)_2O$ to HCl. The stabilization of the nonbonding n_O electrons of $(CH_3)_2O$ associated with the first photoelectron band of the complex is due to a through-space inductive effect associated with an ionic intermolecular hydrogen bond.

Introduction

The study of intermolecular interactions has not been widely canvassed by the ultraviolet photoelectron (PE) spectroscopic technique. In contrast with infrared and Raman spectroscopy and with microwave spectroscopy, it offers the provision of energetic data, for gas-phase molecules, which relate directly to the valence electron bonding properties of an intermolecular species, and allows specific comparisons with the corresponding data for the free molecules involved.

He(I) PE spectroscopy has been used in a number of gas-phase studies of relatively strong intermolecular complexes. Lloyd and Lynaugh[1] obtained the spectra of NH_3BH_3 and BH_3CO, and Lake[2] studied the complexes of BF_3 with the methylamines. Utsunomiya et al.[3] have reported the spectra of complexes of Br_2 with some higher alkylamines. Because of the relatively strong interactions involved in these complexes each was obtained in an undissociated state despite the low vapor pressure regime required for typical PE spectroscopic measurements.

Where weaker intermolecular interactions are involved, the He(I) spectra are complicated by the presence of free molecules in gaseous equilibria which may be unfavorable toward the complexed species. This has been demonstrated by Thomas[4] in reduced-temperature studies on a number of simple carboxylic acids, and by the dimer of NO_2 which has been studied in a number of laboratories[5-9] where effusive nozzle inlet systems and/or reduced temperature was used to produce varying monomer–dimer equilibrium mixtures in the gas phase. A high-pressure gas nozzle inlet system not only samples an equilibrium at elevated pressure but also encourages molecular aggregation via expansive cooling of the gas mixture as it enters the high vacuum of the typical ionization chamber.

For very weak interactions such as occur in the weakly bonded rare gas diatomic molecules, supersonic molecular beams have provided the necessary means of production as shown by the recent He(I) PE studies of Dehmer and Dehmer.[10]

The gas-phase intermolecular complex, or heterodimer, of dimethyl ether and hydrogen chloride has been known for some time, and, though it has been studied by various techniques, it is not well characterized. Lawley and Sutton[11] studied molecular association in gaseous mixtures of $(CH_3)_2O$ and HCl deducing an equilibrium constant for 1:1 heterodimer formation of 0.24 atm^{-1} at 19.5 °C corresponding to an association energy of $\Delta H = -20$ kJ mol^{-1}. In the absence of condensation, equimolar mixtures of $(CH_3)_2O$ and HCl at this temperature hence consist of 0.11 mole fraction of the complex at a total pressure of 1 atm, rising to 0.35 mole fraction at 4 atm.

A number of infrared spectroscopic studies have concluded that a simple bimolecular hydrogen-bonded complex, $(CH_3)_2O{\cdot}HCl$, is present. Temperature-dependent bands have been measured at 2660 and 2470 cm^{-1},[12] the latter being 320 cm^{-1} lower than the stretching frequency of the free HCl molecule. A far-IR band at around 120 cm^{-1} has been identified as the stretching mode of the hydrogen bond of the complex.[13-15] A recent study of the Raman spectrum[16] shows some spectral differences with the corresponding IR data. A ΔH value averaging -31 kJ mol^{-1} has been indicated by variable-temperature IR[13] and NMR[17] studies. There is no evidence that higher clusters of $(CH_3)_2O$ and HCl are formed, though this may be due to the moderate pressures used in most of the above studies. However, Govil et al.[17] reported that partial pressures of $(CH_3)_2O$ greater than 2 atm produced condensation on mixing with HCl.

Experimental Section

The ultraviolet photoelectron spectrometer, which has been specially designed for the study of transient molecular species, has been described in detail elsewhere.[18] It consists of separately pumped ionization and analyzer chambers. The helium discharge lamp is of standard design, and the electron analyzer is a 150° double hemispherical electrostatic focusing type. The spectrometer is controlled by an on-line PDP 11/20 minicomputer which operates a repetitive 1024-point analyzer sweep voltage over any chosen range and counts and stores the pulses from the electron detection and amplification system.

The sample inlet port is designed to accept a variety of interchangeable glass and metal inlet systems. These are normally 6-mm o.d. tubes terminating in nozzles of varying diameters. The nozzle is inserted into a small ionization box within the ionization chamber. This box contains the double slit entry to the electron analyzer, and is evacuated through a number of circular holes. The local vapor pressure in the ionization region is controlled by varying the distance of the nozzle from the photon beam, by closing some of the holes in the ionization box, and by using a small liquid nitrogen cooled cryopump with its working surface situated outside the box 3 cm beyond the ionization region on the opposite side to the inlet nozzle. With very small nozzles stagnation pressures of up to 10 atm can be used while keeping the mean pressure in the ionization box well below the $\sim 10^{-1}$ Torr limit where electron–molecule collisions can interfere with photoelectron transmission.

At 0 °C HCl, with a vapor pressure of over 20 atm, is rather more volatile than $(CH_3)_2O$ at about 2.5 atm. The volatility of the $(CH_3)_2O{\cdot}HCl$ complex is much lower, so the mixing of equimolar amounts of the gases at this temperature results in a considerable drop in pressure generally associated with condensation of the mixture. Unless the temperature is raised above 0 °C, a high-pressure mixture

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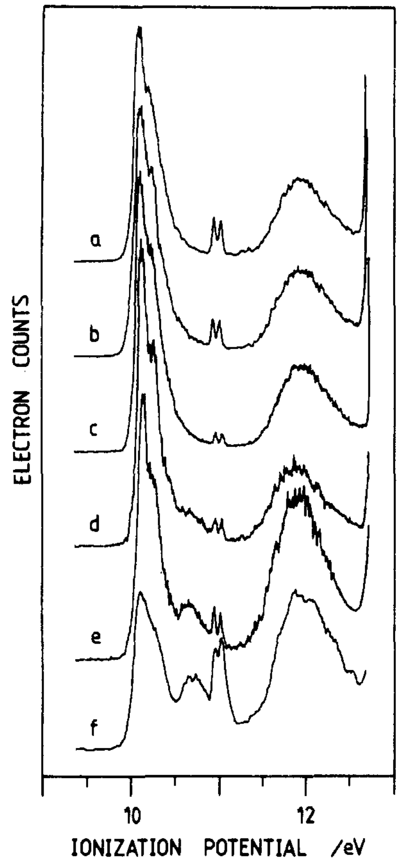

Figure 1. He(I) photoelectron spectra of various $(CH_3)_2O/HCl$ mixtures. Spectra (a)-(c) are for low pumping efficiency in the ionization region; spectra (d)-(f) are for high pumping efficiency. The nozzle diameter and total stagnation pressure for each are (a) 50 μ, 0.3 atm; (b) 50 μ, 2 atm; (c) 15 μ, 3 atm; (d) 10 μ, 0.8 atm; (e) 15 μ, 5 atm; (f) 10 μ, 0.8 atm.

of the two compounds shows a considerable excess of HCl in the vapor phase.

A number of single-sweep He(I) spectra of the 9-13-eV ionization potential range are shown in Figure 1 for $(CH_3)_2O/HCl$ mixtures measured under varying conditions. The broad bands centered near 10 and 12 eV are the first and second bands of $(CH_3)_2O$. The first band of HCl onsets sharply near 12.6 eV, and the excess HCl normally present is indicated by the satellite He(I)β first band of HCl which is the weak doublet peak near 11 eV. The He(I)β peaks are $^1/_{50}$th the intensity of the corresponding He(I)α peaks.

When HCl is added to a sample tube of liquid $(CH_3)_2O$ held at −34 °C, the He(I) spectrum of the vapor above the liquid mixture shows only monomeric $(CH_3)_2O$ and HCl present. Using a 50-μ diameter nozzle and a total stagnation pressure of ~0.3 atm the pressure in the ionization box is around 2×10^{-3} Torr. The spectrum measured under these conditions is shown in Figure 1a. On raising the temperature to −8 °C, the same procedure gives a stagnation pressure of ~2 atm and a relatively larger amount of $(CH_3)_2O$ as shown in Figure 1b. At 8 °C and ~3 atm the amount of $(CH_3)_2O$ is maximized, but with a 15-μ diameter nozzle the spectrum in Figure 1c is that of the monomers only.

Each of these three spectra was obtained by using the cryopump with a relatively closed ionization box. When a relatively open ionization box was used, the liquid nitrogen cooled cryopump could not be used because it caused condensation which blocked the various nozzles. Spectra obtained under these conditions are shown in Figures 1d-f. Each of these shows a new PE band at 10.6 eV. With a 10-μ diameter nozzle and stagnation pressures of around 0.8 atm, the spectra of Figures 1d and 1f are of mixtures containing excess $(CH_3)_2O$ and HCl, respectively. The location of the new band does not vary with the composition of the mixture, and, since it reduces in intensity with a decrease in either $(CH_3)_2O$ or HCl pressure, it is reasonable to conclude that it represents the 1:1 heterodimer of $(CH_3)_2O$ and HCl.

With a larger 15-μ nozzle and a stagnation pressure of ~5 atm, larger count rates result for all species, as represented by the spectrum shown in Figure 1e. When the spectrum of each monomer was measured under the same nozzle and pressure conditions, there was no indication of band changes which would suggest the presence of the respective homodimer species.

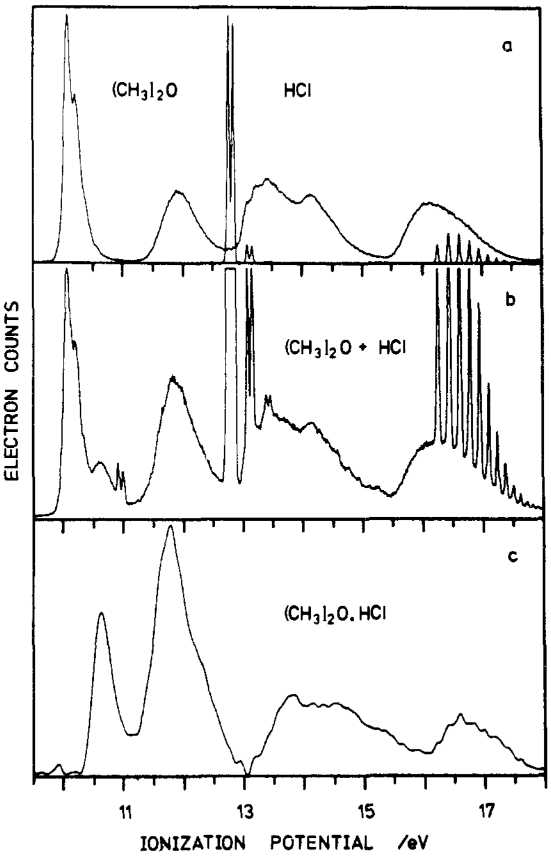

Figure 2. He(I) photoelectron spectra of (a) $(CH_3)_2O$ and HCl, (b) a mixture of $(CH_3)_2O$ and HCl showing the presence of the heterodimer $(CH_3)_2O{\cdot}HCl$, and (c) the heterodimer $(CH_3)_2O{\cdot}HCl$ obtained by spectrum stripping.

To avoid the possible formation of higher clusters the mixture chosen for time averaging was that represented by the spectrum in Figure 1e. In terms of band areas this mixture was estimated to contain 10% of complexed $(CH_3)_2O$. The time-averaged spectra of 1024 points are shown in Figure 2. The superimposed spectra of $(CH_3)_2O$ and HCl in Figure 2a were obtained at count rates similar to those represented in the ~5-atm equilibrium mixture of $(CH_3)_2O$ and HCl shown in Figure 2b. Each time-averaged run was of 2-h duration, and the IP calibration was based on the known IPs of the monomers and utilized the He(I)α-He(I)β energy spacing.

As well as the heterodimer band centered at 10.6 eV, the other obvious feature of the spectrum in Figure 2b is that the bands centered near 11.8 eV show a different relative intensity to the first band of $(CH_3)_2O$ in comparison with the second band of $(CH_3)_2O$ in Figure 2a. Clearly there are heterodimer bands in this region as well.

Analysis

Spectrum stripping or subtraction is an important aspect of the spectroscopic study of mixtures. In various forms it has been utilized in photoelectron spectroscopic studies of radicals,[19] of surface-adsorbed molecules,[20] and of molecular conformers.[21,22] We have developed an interactive spectrum stripping computer program which utilizes spectrum display facilities. This has been used in studies of transient or reactive molecules in gaseous mixtures. Its earliest use was to obtain the He(I) spectrum of CH_2NH from that of a mixture that otherwise consisted of the stable species CH_3NH_2, HCN, and H_2.[23] More recently we have obtained the He(I) spectra of CH_3NHBr and CH_3NBr_2 by analyzing different mixtures of these with the reactants CH_3NH_2 and Br_2.[24] A He(I) spectrum of the very reactive $NHBr_2$ has been obtained by spectrum stripping of a mixture estimated to contain only 2% of the transient species.[25]

The spectrum-stripping program allows the user to choose any linear combination of any number of time-averaged PE spectra and to assess its features by means of visual display of the resulting spectrum. Specific features of the program allow the shifting of any spectrum to either left or right and the broadening or smoothing of any spectrum.

Spectrum shifting is necessary because of variations in the positions of calibration points in different spectra. These result from unavoidable variations in surface potentials and pressure shift effects in measuring different gas mixtures. Any spectrum can be convoluted by a normalized Gaussian function of chosen half-width. Spectrum broadening is necessary because there are real differences in the operational instrumental resolution of different measured spectra. This is the result of the varying surface adsorption characteristics of different gases and their effect on surface potentials in the proximity of the electron trajectories. A stripped spectrum is often rather noisy, particularly if it represents a component of low proportion in a mixture, so it is useful to smooth a calculated spectrum using a chosen Gaussian convolution.

A relatively uncomplicated visual assessment made by the program user is that associated with the removal of a simple spectrum, say of a diatomic molecule, from a mixed spectrum. A more complicated judgment involves the identification of different bands which belong to the same species due to their similar behavior during a stripping procedure.

The subjectivity of this spectrum-stripping method can be questioned because the experience and skill of the user are obviously factors in its successful application. However, in the absence of precise numerical criteria for such techniques, the visual spectrum stripping method can only be judged by its results. An example of this is the He(I) spectra of the reactive haloamines NH_2Cl and CH_3NHCl, where our stripped spectra[26,27] compare very well with the spectra obtained by Colbourne et al. using the pure compounds.[28,29]

The spectrum stripping of the $(CH_3)_2O$ and HCl shown in Figure 2a from the mixed spectrum of Figure 2b is reasonably straightforward. The removal of the sharp HCl bands is easy to assess but is made difficult by the sharpness of the peaks which requires perfect alignment of the two spectra. Imperfections in this stripping are seen in the ripples remaining on the otherwise unstructured bands in Figure 2c. The removal of the $(CH_3)_2O$ spectrum relies on the assumption that there is no band of another species located near the low ionization potential (IP) side of the first band of $(CH_3)_2O$ at 10 eV. The resulting stripped spectrum is noisy in places, so smoothing of the 1024-point spectrum with a Gaussian of half-width 4 points gives the result shown in Figure 2c. This spectrum is assigned as that of the heterodimer $(CH_3)_2O \cdot HCl$. The appearance of this spectrum is consistent with the earlier observations of the new PE band appearing at 10.6 eV and the intensity enhancement of the bands at 11.8 eV. The higher IP bands beyond 13 eV, though not revealed in the mixed spectrum of Figure 2b, are observed to be essentially the higher bands of $(CH_3)_2O$ shifted fairly uniformly upwards in IP.

Calculations

It is probably due to the paucity of experimental data that the $(CH_3)_2O \cdot HCl$ complex has not been widely studied theoretically. In particular, of the many recent molecular orbital studies on intermolecular species, only one series of calculations is available for $(CH_3)_2O \cdot HCl$. Hinchliffe[30] has presented SCF-MO results using basis sets of different levels of sophistication. The calculations were based on essentially planar structures with the H and Cl atoms lying along the C_2 symmetry axis of the $(CH_3)_2O$ molecule. This was assumed on the basis of earlier studies on the IR data by Coulson and Robertson.[31] However, experimental and theoretical studies on various other hydrogen-bonded homodimers and heterodimers suggest that $(CH_3)_2O \cdot HCl$ is unlikely to be planar. Hence variation of the out-of-plane angle of the linear O-H-Cl arrangement would be a worthwhile addition to these studies.

Hinchliffe found that both the calculated equilibrium bond length, R(O-H), and the hydrogen-bond energy, ΔH, of the complex changed dramatically with increasing size of the basis set. In going from an STO-3G to an STO-4-31G to a Dunning contracted basis, R(O-H) increased from 1.46 to 1.68 to 1.97 Å, whereas ΔH decreased from 49 to 41 to 22 kJ mol^{-1}.

We have used the GAUSSIAN 70 molecular orbital program and the STO-3G minimum basis for calculations on $(CH_3)_2O \cdot HCl$ for various geometries of C_s symmetry. With the $(CH_3)_2O$ and HCl moieties fixed at their experimental geometries,[32,33] the O-H-Cl arrangement was kept linear, but varied in the angle made with the C-O-C plane. Within these constraints the geometry optimization leads to an O-H bond length of 1.54 Å and an out-of-plane angle of 34°. This result shows a similar O-H bond collapse to that obtained by Hinchliffe,[30] though our calculations suggest that the heterodimer is likely to be nonplanar. The calculated total energy is not very sensitive to variation of the out-of-plane angle and the equilibrium nonplanar geometry in our calculation is only 1 kJ mol^{-1} more stable than the corresponding planar case.

However, the calculated MO eigenvalues are a sensitive function of the O-H bond length, though not of the out-of-plane angle. At short bond lengths the uppermost occupied MO of the complex is one of the near-degenerate HCl π orbitals, but increasing bond length results in an orbital crossover so that the $(CH_3)_2O$ MO of localized n_O character becomes uppermost. Since we wish to use the Koopmans approximation as the link between the MO results and the PE spectrum of the heterodimer, and since the uppermost MO of the complex is clearly associated with the n_O orbital, then the shorter O-H bond length is inappropriate. A value of 1.9 Å was chosen as a reasonable value for further calculations.

Moreover, since we want the calculations, elementary though they are, to correlate with the description of the effects of intermolecular complexation on each of the monomers involved, another problem associated with the minimum basis needs correction. This is the observation that the minimum basis performs less adequately for HCl than it does for $(CH_3)_2O$ in that within the Koopmans approximation the HCl MOs lie too high in energy relative to the $(CH_3)_2O$ MOs as represented experimentally by the vertical IP data. Orbital relaxation and many-body correlation effects are no doubt different for these two molecules and may offer some explanation for this observation. However, for the purpose of this study, it was found that a small extension of the Cl basis set, by the addition of 1s, 2s, and 2p STOs each of exponent 1.4, stabilized the HCl valence MOs by the required amount averaging 0.8 eV.

The corresponding Koopmans IPs obtained with this STO-3G* basis set for the $(CH_3)_2O \cdot HCl$ complex with an O-H bond length of 1.9 Å and an out-of-plane angle of 34° are listed in Table I, where they are compared with the experimental vertical IPs of the heterodimer obtained from Figure 2c. Scaled Koopmans IPs obtained from Hinchliffe's extended basis calculation[30] are also given.

Discussion

For the $(CH_3)_2O \cdot HCl$ heterodimer there is generally good agreement between the observed and calculated patterns of IPs. However, the effects of complexation are perhaps better shown by a comparison of the monomer and dimer IPs as indicated

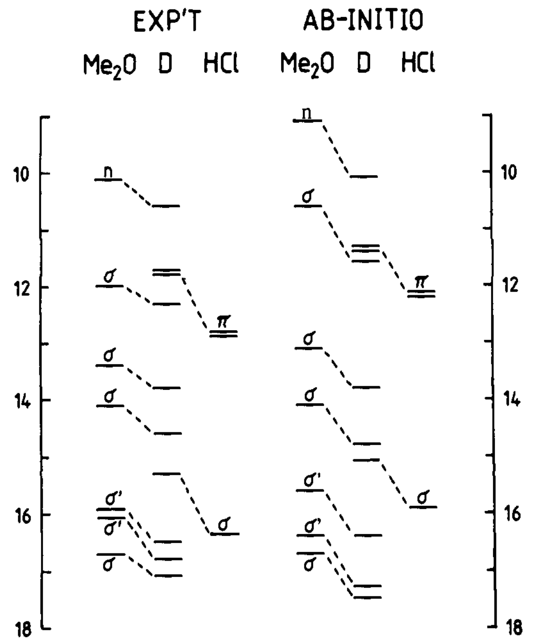

Figure 3. Correlation diagrams of the vertical ionization potentials (eV) of the monomers and dimer of $(CH_3)_2O{\cdot}HCl$. The experimental values are compared with calculated data from the GAUSSIAN 70 STO-3G* molecular orbital calculations. For $(CH_3)_2O$ the σ and σ' ionizations are referred to in the text as σ_{CH_3} and σ_{CO}, respectively.

in Figure 3, where the experimental and calculated IP shifts are illustrated by the appropriate correlation diagrams.

The experimental data indicate that the effect of hydrogen-bond formation is to raise the n_O IP of $(CH_3)_2O$ by 0.6 eV and to lower the π_{Cl} IPs of HCl by 1.0 eV. The σ_{CH_3} IPs are increased by an average of 0.4 eV on dimerization, with the σ_{CO} IPs raised by a mean of 0.7 eV. The STO-3G* calculations show more uniform IP shifts with the HCl Koopmans IPs being lowered by an average of 0.8 eV and those of the $(CH_3)_2O$ orbitals being raised by amounts ranging from 0.7 to 1.0 eV. For $(CH_3)_2O$ the shifts increase with closer proximity of the orbital to the HCl moiety. Though the HCl shifts are underestimated and the $(CH_3)_2O$ are overestimated, the general agreement between the experimental and calculated IPs as shown in Figure 3 indicates that the STO-3G* wave functions offer a fair description of the effects of heterodimer formation. By contrast Hinchliffe's extended basis calculation[30] gives scaled (by −0.9) Koopmans IP shifts which are in good agreement with the experimental data for the $(CH_3)_2O$ moiety but underestimate the HCl shifts.

An interesting property of the heterodimer is the net transfer of electron density from $(CH_3)_2O$ to HCl. This information is not directly available from the PE data, but it can be estimated using a simple quantitative description of an inductive effect causing a shift in IP. The formula $\Delta q = \Delta I/I_0$ follows from the approximation that the IP gradient, $\Delta I/\Delta q$, of IP as a function of local charge density is equal to the free IP, I_0, of the atom or group concerned.[32] Since the π_{Cl} and σ_{CH_3} orbitals are those least associated with the intermolecular hydrogen bond in the $(CH_3)_2O{\cdot}HCl$ complex, their IP shifts can be regarded as due to inductive movement of electron density from $(CH_3)_2O$ to HCl. Hence IP gradients of 14.2 eV/e for CH_3 and 13.0 eV/e for Cl lead, via the experimental IP shifts, to a 0.03-e loss from each CH_3 and a 0.07-e gain by Cl. These are in excellent agreement with the STO-3G* calculated values of a 0.03-e loss by each CH_3 and a 0.08-e gain by Cl. According to the MO data, the O atom gains only 0.01 e and the H atom loses 0.03 e, the total net transfer amounting to 0.05 e from $(CH_3)_2O$ to HCl. Hinchliffe's extended basis calculation[30] shows a corresponding shift of only 0.01 e to HCl.

Table I. Experimental Vertical Ionization Potentials and Assignment of the $(CH_3)_2O{\cdot}HCl$ Heterodimer Compared with Calculated Ionization Potentials (eV)

exptl[a]	assignment MO (C_s)	STO-3G* ($-\epsilon$)	ext basis[b] (-0.9ϵ)
10.6	15a′ (n_O)	10.05	10.78
11.8	14a′ (π_{Cl})	11.37	10.92
11.8	7a″ (π_{Cl})	11.38	10.96
12.3	13a′ (σ_{CH_3})	11.51	12.17
13.8	6a″ (σ_{CH_3})	13.84	13.38
14.6	5a″ (σ_{CH_3})	14.77	13.95
15.3	12a′ (σ_{HCl})	15.06	14.58
16.5	4a″ (σ_{CO})	16.45	15.95
16.8	11a′ (σ_{CO})	17.26	16.58
17.1	10a′ (σ_{CH_3})	17.51	16.61

[a] Accuracies vary between ±0.05 and ±0.2 eV. [b] From ref 30.

A comparison of the STO-3G* MOs of the heterodimer and the two monomers shows that there is virtually no change in the AO contribution to any MO due to complexation, the electron-density transfer being so small. The σ_{HCl} MO shows the slight adjustment due to electron density passing from H to Cl, but covalent interaction with any O orbitals is not involved. The clear conclusion from this analysis is that the interaction between the two monomers is basically ionic in nature, and that the IP shift of the n_O orbital, in particular, is due to a through-space inductive effect. The STO-3G* atomic charge on the H atom of HCl is +0.17, which at a distance of 1.9 Å produces a potential of 1.3 eV at the O atom. This can be regarded as the main contribution to the 1.0-eV lowering of the eigenvalue of the n_O orbital in going from $(CH_3)_2O$ to $(CH_3)_2O{\cdot}HCl$.

Conclusion

The He(I) photoelectron spectrum of the gas-phase heterodimer of $(CH_3)_2O$ and HCl has been interpreted with the aid of GAUSSIAN 70 molecular orbital calculations. Analysis of the IP shifts occurring on dimerization indicates an inductive transfer of about 0.05 e from $(CH_3)_2O$ to HCl. The 0.6-eV stabilization of the nonbonding n_O electrons of $(CH_3)_2O$ is shown to be due to a through-space inductive effect associated with ionic character of the intermolecular hydrogen bond of the complex.

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Theoretical Study of the Reaction of Water with the 1,3 Dipoles Fulminic Acid and Acetonitrile Oxide. Concerted Reactions with a Proton Slide at the Transition State[1]

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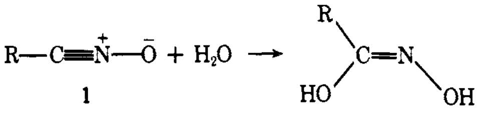
Abstract: The ease of deformation of fulminic acid (HCNO) and acetonitrile oxide (CH_3CNO), the formation of hydrogen-bonded complexes with water, and the reaction pathway with water as nucleophile ($RCNO + H_2O \rightarrow RC(OH){=}NOH$) have been studied using the ab initio method. The calculations were carried out using Roothaan's LCAO-SCF-MO and the supermolecule technique, using Pople's STO-3G basis set. The reaction pathways were studied by allowing six angles and five bond distances to vary, using the distance R between the carbon of the 1,3 dipole and the oxygen of the water molecule as reaction coordinate. Fulminic acid is most easily bent in the E (or trans) direction and this is the configuration induced in the transition state as the water molecule approaches (thus determining the stereospecific nature of the reaction, as observed experimentally). As the transition state is reached (R = 1.85 Å) there is no energy barrier for the transfer of a proton from the oxygen of the attacking water molecule to that of the fulminic acid. The stereospecificity of the reaction thus ensures that the two oxygens are correctly oriented to facilitate this "proton slide". There are no intermediates on the reaction pathway which can thus be described as a concerted but asynchronous ($4\pi + 2s$) reaction. Acetonitrile oxide is less reactive (activation energy of 29.2 relative to 23.5 kcal mol^{-1} for fulminic acid) and the transition state is reached later with both more proton transfer and deformation of the 1,3 dipole. With HCNO two H-bonded complexes can be formed with water (which do not lie on the reaction pathway); the relative stabilities and the isomerization between the conformations of product hydroxyformaldoxime are also reported.

Nitrile oxides (**1**), which are propargyl-type 1,3 dipoles, react not only with unsaturated substrates (2π systems) to give five-membered heterocycles,[3] but also with nucleophilic reagents, including both anionic (such as HO^-, CH_3O^-, N_3^-, etc.) and neutral (H_2O, ROH, R_2NH, etc.) examples.[4] This latter addition leads to the formation of open-chain oximes as products.

The mechanism of the reaction of alkenes with 1,3 dipoles has been the subject of intensive study and there now appears to be agreement that this is generally a concerted reaction in which the bonds to the two termini of the dipolarophile are formed at or about the same time.[3] The reaction of RCNO with nucleophiles occurs by attack at carbon; however, these reactions also appear to be stereospecific in that only one of the two possible oxime isomers in invariably formed.[4] We have previously reported[5] that this experimental result is confirmed in a model reaction—that of hydroxide ion (HO^-) with fulminic acid (HCNO). In this case it was shown that the Z form of the product was determined kinetically at the transition state—the configuration of the product was independent of any interaction between the oxygen of the 1,3 dipole and the incoming nucleophile (which was minimal).

In neutral solution (pH < 8), water reacts with benzonitrile oxide (**1**, R = Ph) and related 1,3 dipoles.[4] The reaction is slow ($t_{1/2} > 100$ min) and was shown to be pH independent. Substituent effects suggest that water is also acting as a nucleophilic reagent.



$$R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O} + H_2O \longrightarrow R(HO)C{=}NOH$$

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We have now carried out a theoretical study on this reaction using both fulminic acid (**1**, R = H) and acetonitrile oxide (**1**, R = CH_3) as substrates. We were particularly interested in this case in the timing of proton-transfer relative to the movement of heavy atoms and in the possibility that both processes could be concerted.

Methods of Calculation

The calculations were carried out by the ab initio method of Roothaan.[6] In each case we have utilized the STO-3G basis set of Pople[7a] with the GAUSSIAN-70 program.[7b] This basis set is sufficiently reliable for studying reactions between neutral molecules. Moreover, it is not necessary to include a limited configurational interaction in order to obtain qualitatively significant results, since the number of pairs of electrons is conserved in the course of reaction. We have adopted the

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