Chemical Dynamics. Tritiated Boc-valine was prepared by reacting valine-G-^3H with di-tert-butyl dicarbonate (Fluka).[44] p-Tolylacetic acid, N-(hydroxymethyl)phthalimide, and bromoacetophenone were obtained from Aldrich. Methylene chloride was distilled over sodium carbonate. DMF was MCB spectroquality and was stored over 4 Å molecular sieves. The materials and methods for solid-phase synthesis were similar to those described elsewhere[16] but modified as indicated. Hydrolysis of peptide-resins to amino acids was done by using 12 N HCl–propionic acid (1:1 v/v)[18] at 130 °C for 6 h with norleucine as the internal standard. Ion exchange chromatography was performed on a Beckman amino acid analyzer (Model 121). Buffers were prepared from Beckman concentrates.

Aminomethyl-resin of the desired substitution was prepared by the procedure of Mitchell et al.[16] Two batches of resin were prepared containing 0.31 (0.22 mmol/g) and 1.31% N (0.95 mmol/g), respectively, by elemental analysis. tert-Butoxycarbonylvalyl-4-(oxymethyl)phenyl-acetic acid was prepared as previously described,[45] isolated as the free acid, and recrystallized from ethyl acetate–petroleum ether to give a pure white solid, 76% yield, mp 72–74 °C.

Anal. Calcd: C, 62.46; H, 7.39. Found: C, 62.56; H, 7.38.

This product was used to prepare tert-butoxycarbonylvalyl-4-(oxymethyl)phenylacetamidomethyl-resin (Boc-Val-Pam-Res), as described previously.[16]

Synthesis of Boc-Leu-Ala-Gly-Val-OCH₂-Pam-Resin. The following protocol was used for the synthesis of the model tetrapeptide. Boc-L-Val-OCH₂-Pam-resin (1 g) was placed in a reaction vessel and for the introduction of each amino acid was treated with shaking with the following reagents for the times shown, followed by filtration: (1) 20 mL of CH₂Cl₂ (3 × 1 min); (2) 20 mL of trifluoroacetic acid–CH₂Cl₂ (1:1 v/v) (1 min); (3) 20 mL of trifluoroacetic acid–CH₂Cl₂ (1:1 v/v) (30 min); (4) 20 mL of CH₂Cl₂ (6 × 1 min); (5) 20 mL of 5% diisopropylethylamine in CH₂Cl₂ (5 min); (6) 20 mL of CH₂Cl₂ (3 × 1 min); (7) 20 mL of 5% diisopropylethylamine in CH₂Cl₂ (5 min); (8) 20 mL of CH₂Cl₂ (3 × 1 min); (9) Boc-Gly-OH (4 equiv) in 15 mL of CH₂Cl₂ (5 min), without filtration, followed by (10) DCC (4 equiv) in 5 mL of CH₂Cl₂ for 30 min; (11) 20 mL of CH₂Cl₂ (6 × 1 min). This synthetic cycle was repeated with Boc-L-Ala and then with Boc-L-Leu. In a double-coupling synthesis, steps 7–11 were repeated in each cycle. Successive LAGV-OMPA units were assembled by the above procedures.

Density Measurements of Dry Resin Samples. Unsubstituted copoly-(styrene–1% divinylbenzene) resin (Biobeads S-X1, 200–400 mesh) (0.541 g) was weighed in a graduated conical centrifuge tube. Petroleum ether (30–60 °C) was added to just cover the beads and allowed to equilibrate for 1 h. The weight of added solvent was determined to be 0.326 g and the total volume of the mixture was 1.05 mL. From the density of petroleum ether (0.65 g/mL) the volume of solvent was 0.50 mL and therefore the volume of the resin was 0.55 mL, giving a density of 0.98 g/mL. By microscopic examination it was shown that no swelling of the beads occurred in this solvent. The densities of the peptide-resins were determined in the same way.

(44) D. Stanley Tarbell, Y. Yamamoto, and B. M. Pope, Proc. Natl. Acad. Sci. U.S.A., 69, 730 (1972).

(45) J. P. Tam, S. B. H. Kent, T. W. Wong, and R. B. Merrifield, Synthesis, 955 (1979).

Dipole-Supported States. A Very Low Lying Excited State of Acetaldehyde Enolate Anion

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Abstract: The potential surfaces of the ground-state anion, ground-state radical, and lowest excited anion states of acetaldehye enolate have been investigated by ab initio SCF calculations and configuration interaction. A (9s5p/4s2p) Dunning–Huzinaga basis set, augmented with 3s and diffuse p atomic orbitals, and in some cases with polarization functions, has been used. A low-energy Rydberg-like excited anion has been found, lying 1.82 eV above the anion ground state, after zero-point energy correction. This excited state is very similar to the ground state of the neutral radical, and is probably responsible for the sharp resonances observed in electron photodetachment experiments.

Introduction

Threshold resonances in the photodetachment cross sections of substituted acetophenones and acetaldehyde enolate anions have recently been reported.[2,3] Substituent effects, as well as semiempirical calculations,[3] do not support the hypothesis that these resonances are conventional n–π* or π–π* excited states. For this reason, an explanation based on the possibility of low-lying, dipole-supported excited states of the anions was suggested.[3] Photodetachment would then be enhanced by excitation of the anion to vibrational levels of this first excited state. If weakly coupled to the continuum, this state would account for the observed sharp resonances.

Dipole-supported states have received considerable theoretical[4–18] attention. It has been shown that a fixed dipole may bind an electron, provided that the dipole moment is greater than the critical value 1.625 D. Crawford[7] and Garrett[8] have analyzed critical values more adapted to real molecules. Taking into account

(1) (a) University of California, Berkeley. (b) Stanford University.

(2) Zimmerman, A. H.; Brauman, J. I. J. Chem. Phys. 1977, 66, 5823.

(3) Jackson, R. L.; Zimmerman, A. H.; Brauman, J. I. J. Chem. Phys. 1979, 71, 2088.

(4) Wallis, R. F.; Herman, R.; Milnes, H. W. J. Mol. Spectrosc. 1960, 4, 51.

(5) Levy-Leblond, J. M. Phys. Rev. 1967, 153, 1.

(6) Crawford, O. H. Proc. Phys. Soc., London 1967, 91, 279.

(7) Crawford, O. H. Mol. Phys. 1971, 20, 585.

(8) Garrett, W. R. Mol. Phys. 1972, 24, 465.

(9) Jordan, K. D.; Wendoloski, J. J. Chem. Phys. 1977, 21, 145.

(10) Jordan, K. D. J. Chem. Phys. 1977, 66, 3305.

(11) Jordan, K. D. J. Chem. Phys. 1976, 65, 1214.

(12) Jordan, K. D.; Griffing, K. M.; Kenney, J.; Andersen, E. L.; Simons, J. J. Chem. Phys. 1976, 64, 4730.

(13) Jordan, K. D.; Luken, W. J. Chem. Phys. 1976, 64, 2760.

(14) Jordan, K. D.; Wendoloski, J. J. Mol. Phys. 1978, 35, 223.

(15) Garrett, W. R. Phys. Rev. A 1971, 3, 961.

(16) (a) Garrett, W. R. J. Chem. Phys. 1978, 69, 2621. (b) Ibid. 1979, 71, 651. (c) Chem. Phys. Lett. 1979, 62, 325.

(17) Crawford, O. H.; Garrett, W. R. J. Chem. Phys. 1977, 66, 4968.

(18) Jordan, K. D. Acc. Chem. Res. 1979, 12, 37, and references cited therein.

Excited State of Acetaldehyde Enolate Anion

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rotational motion, Garrett[15] has found a critical dipole moment 10–30% larger than 1.625 D, while Crawford[7] has estimated the value 2.5 D as a lower limit. However, the simple dipole model turns out to be quantitatively rather poor, according to the recent ab initio calculations of Jordan,[9–14] using quite flexible basis sets. These calculations have been performed for a series of polar molecules, and they show that the electron affinities estimated by Koopmans' theorem (KT) are in poor agreement with predictions of the dipole model, the latter being wrong by factors ranging from 0.13 to 24. Nevertheless, Jordan[11,14] has noted a rough linear correlation between calculated dipole moments and electron affinities. Many ab initio calculations underestimate electron affinities owing to lack of electron correlation. Indeed, Garrett[16a,b] has noted that induced dipole forces, poorly accounted for by Hartree–Fock calculations, make very important contributions to the binding of electrons; Jordan,[12] introducing correlation by the equations-of-motion method, has estimated (KT) electron affinities to be too small by 0.05–0.15 eV, at least for very polar molecules.

The applicability of the electron–dipole theory has been justified on a number of bases, and indeed Garrett has suggested[16c] that such states must exist in the Born–Oppenheimer approximation. Nevertheless, the inability to observe such states experimentally[19] raises serious questions, as do the ab initio calculations for ground states which are numerically in rather poor agreement with the dipole model. We have previously suggested[3] that dipole-supported states, which are likely to be weakly bound at best, may exist as excited states of stable, strongly bound anions. However, no quantum-mechanical calculation addressing the existence of such excited states has yet appeared.

Dipole moments of the neutrals of the enolates which exhibit resonances attributed to dipole-supported excited states have been calculated[3] by the INDO method to range from 1.8 to 2.3 D. These values are too small and too unreliable to be conclusive regarding the possibility of dipole-supported states; thus, we have investigated the low-lying excited states of the enolate anions by means of ab initio methods using a large basis set. We took as a model the acetaldehyde enolate anion, the smallest of the enolate anions which show resonances.[20] We did not attempt to calculate directly the electron affinity of the neutral enolate by comparing its energy with the ground state of the anion. Such a calculation, comparing molecules with different numbers of electrons, would necessitate a basis set and a level of configuration interaction which are prohibitive because of the size of the molecule. Rather, we attempted to compare the energy gap between the lowest lying excited state of the anion and its ground state with the accurate experimental value[20] 1.827 ± 0.005 eV separating the radical ground state from the anion ground state. An energy gap smaller than this value means that there exists a loosely bound excited state of the acetaldehyde enolate anion. Whether or not this state is "dipole supported" may be known by examination of the highest occupied orbital of the excited anion and the dipole moment of the neutral.

Quantum-Mechanical Methods

For the SCF calculations, we have used an augmented standard Dunning–Huzinaga double ζ (DZ) contracted Gaussians basis set,[21,22] labeled as (9s5p/4s2p) for carbon and oxygen and (4s/2s) for hydrogen. We added 3s functions, with exponents 0.021 and 0.032 for carbon and oxygen, respectively, to allow for and describe properly a possible Rydberg-like state; furthermore, to describe the expanded orbitals of the negative ions, we added diffuse p

Table I. Equilibrium Geometries for the Ground Anion, Radical, and Excited Anion States

	ground anion	radical	excited anion
CC bond length^a	1.377	1.459	1.453
CO bond length^a	1.303	1.227	1.235
γ angle^b	127.3	122.1	123.0

^{a} Angstroms. ^{b} Degrees.

Table II. Calculated Force Field Matrix Elements^a

|	ground anion	radical	excited anion
f_{CO-CO}	7.20	10.10	10.13
f_{CO-CC}	-0.07	1.34	1.34
f_{CC-CC}	7.46	6.23	6.17
$f_{\gamma-\gamma}$	1.94	2.04	2.04
$f_{\gamma-CO}$	0.17	-0.08	-0.09
$f_{\gamma-CC}$	0.22	0.25	0.09

^{a} Units are mdyn/Å, mdyn/rad, mdyn·Å/rad^2.

functions[23] to carbon and oxygen, with exponents 0.034 and 0.059, respectively. For the equilibrium geometry of the radical state, the basis set was further augmented with five d-polarization functions on each carbon and oxygen, with exponents 0.75 and 0.85, respectively. Thus, the numbers of primitive Gaussians and contracted basis functions are 96 and 48, respectively, for the DZ basis set, and 111 and 63 for the (DZ + P) basis set, involving additional polarization functions. The SCF calculations were performed on the Harris Slash Four minicomputer,[24] using a modified POLYATOM program.[25]

The energies at SCF equilibrium geometry of both anion states have been calculated with configuration interaction (CI) in the SD interacting space. This is achieved by including in the CI all configurations corresponding to single and double excitations from the occupied set to the virtual set of molecular orbitals, the five lowest and the three highest orbitals being excluded. No a″ is excluded from the CI. The number of such configurations is 10 380 for the anion ground state, and 13 666 for the excited anion state. The contributions to energy lowering by higher excitations have been estimated by Davidson's many-body perturbation method.[26] These CI calculations have been performed with the BERKELEY system of programs.[27] While a closed-shell formalism has been used for the anion ground state, both radical and excited anion open-shell states have been examined with the restricted Hartree–Fock method.[28]

Potential-Energy Surfaces

Two resonance formulas (I and II) may be drawn for the
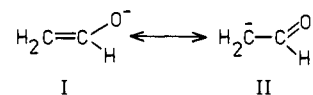
acetaldehyde enolate anion; the radical may also be described by I ↔ II, with an unpaired electron rather than the negative charge. In order to find the true minima, we calculated three full two-dimensional potential surfaces, one for each state, the coordinates being CC and CO bond lengths, with the ∠CCO angle (γ) being

(19) Recent results of Lineberger and co-workers indicate that even alkali halides, MX, with their extremely large dipole moments give negative ions, MX⁻, better described as a neutral alkali adjacent to a halide than as an electron loosely bound to MX: Novick, S. E.; Jones, P. L.; Mulloney, T. J; Lineberger, W. C. *J. Chem. Phys.* **1979**, *70*, 2210. Also, Carlsten, J. L.; Peterson, J. R.; Lineberger, W. C. *Chem. Phys. Lett.* **1976**, *37*, 5. However, see Rohr, K; Linder, F. *J. Phys. B* **1976**, *9*, 2521, for experimental evidence of transient dipole-supported states in scattering experiments.

(20) Jackson, R. L.; Brauman, J. I., manuscript in preparation.

(21) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(22) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(23) Dunning, T. H.; Hay, P. J. In "Modern Theoretical Chemistry", Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, p 9.

(24) (a) Pearson, P. K.; Lucchese, R. R.; Miller, W. H.; Schaefer, H. F. In "Minicomputers and Large Scale Computations," ACS Symposium Series No. 57, American Chemical Society: Washington, D.C., 1977. (b) Schaefer, H. F.; Miller, W. H. *Comput. Chem.* **1977**, *1*, 85.

(25) Neumann, D. B.; Basch, H.; Basch, H.; Kornegay, R. L.; Snyder, L. C.; Moskowitz, J. W.; Hornback, C.; Liebmann, S. P. "POLYATOM 2", QCPE No. 199, Indiana University, Bloomington, Ind., 1972.

(26) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61. Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1978**, *52*, 403.

(27) (a) Lucchese, R. R.; Schaefer, H. F. *J. Chem. Phys.* **1978**, *68*, 769. (b) Lucchese, R. R.; Brooks, B. R.; Meadows, J. H.; Swope, W. C.; Schaefer, H. F. *J. Comput. Phys.* **1978**, *26*, 243.

(28) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.
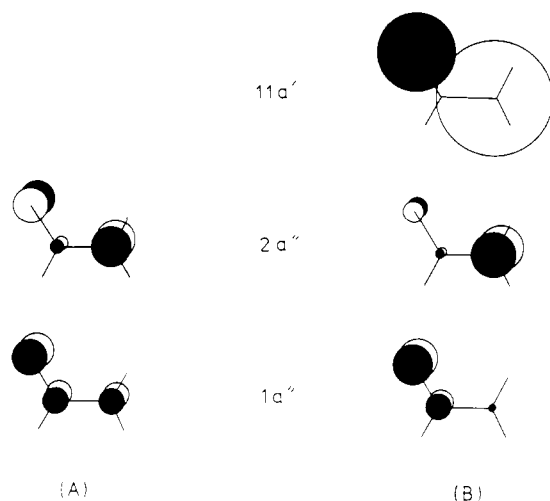
Figure 1. Highest occupied molecular orbitals of acetaldehyde enolate: (A) ground anion state; (B) lowest excited anion state.

fixed at 120°. Then, for each true minimum of these surfaces, the ∠CCO angle has been optimized. Finally, an extra degree of freedom has been investigated for each surface, so as to obtain the parameters γ-CO and γ-CC, necessary to have a force-field matrix for each state (see Table II). One further motivation for obtaining these off-diagonal force field parameters is to allow a more accurate location of the equilibrium geometries. Other parameters have been kept standard, with the value 120° for the ∠HCC angles and 1.08 Å for the CH bond lengths.

Results

To determine the equilibrium geometries and the force-field matrices, we have fit our calculated potential surfaces to quadratic surfaces:

$$2V = f_{CO-CO}(\Delta CO)^2 + f_{CC-CC}(\Delta CC)^2 +$$
$$2f_{CO-CC}(\Delta CO \Delta CC) + f_{\gamma-\gamma}(\Delta \gamma)^2 + 2f_{\gamma-CO}(\Delta \gamma \Delta CO) +$$
$$2f_{\gamma-cc}(\Delta \gamma \Delta CC) \quad (1)$$

where V is the potential energy, and ΔCO, ΔCC, and $\Delta \gamma$ are the deviations from equilibrium geometry of the CO bond length, the CC bond length, and the ∠CCO angle. The resulting equilibrium geometries are displayed in Table I and the force field matrix elements in Table II. It should be kept in mind that the off-diagonal force constants $f_{CO-CC}, f_{\gamma-CO}$, and $f_{\gamma-CC}$ are rather sensitive to the choice of points on the surfaces incorporated into the least-squares fitting equations, while the equilibrium geometries and the diagonal elements are not. The force-field matrices shown here correspond to regions of the surfaces close to the equilibrium geometries.

The highest occupied orbitals for the equilibrium geometries of both anion states are shown in Figure 1. The orbitals of the radical are similar to those of the excited anion state.

A. Anion Ground State. The occupancy for this state is $1a''^2 2a''^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 8a'^2 9a'^2 10a'^2 1a''^2 2a''^2$. The $1a''$ and $2a''$ orbitals (see Figure 1) strongly resemble the π-bonding and π-nonbonding orbitals of an allyl anion. Furthermore, both CO and CC bond lengths are intermediate between single and double bonds. This suggests a strongly delocalized structure, further confirmed by the Mulliken population analysis, which predicts the negative charge to be equally shared by the CH₂ group and the oxygen. The calculated energies are $-152.270\,12$ hartrees at the SCF level, $-152.452\,44$ hartrees after completion of the CI, and $-152.468\,13$ hartrees after Davidson's correction.

B. Anion Excited State. The lowest anion excited state is obtained by exciting an electron from the $2a''$ orbital to the Rydberg-like $11a'$ orbital. This orbital is composed mainly of a 3s atomic orbital on the CH₂ group and another 3s orbital, with a smaller coefficient, on the oxygen.

Surprisingly, these two 3s atomic orbitals are combined in an antibonding way.[29] Such nodes have also been observed by

Jordan[12,13] in the highest occupied orbitals of other weakly bound negative ions of polar molecules. The result of this mixing is to push some electron density away from the center of the molecule, thus reducing electronic repulsion. We believe that this is an indication that the lowest excited state of the acetaldehyde enolate anion is dipole supported.[16c] Indeed, the dipole model becomes realistic when the loosely bound electron is far from the neutral polar molecule. The $1a''$ and $2a''$ orbitals are somewhat modified with respect to those of the ground state, and are located respectively on the CO and CH₂ fragments. The equilibrium geometry is also modified by the excitation, being now typical of II, with a CO double bond and a CC single bond. As expected, the Mulliken population analysis indicates that the charge is largely on the CH₂ group, although charge location with such a diffuse orbital is rather crude. The calculated energies of this state, at the SCF and CI level, are respectively $-152.218\,08$ and $-152.385\,06$ hartrees. Davidson's correction further lowers this value to $-152.399\,40$ hartrees.

Conventional excited n→π* and π→π* states have been found higher in energy. The energy gap between the ground state and the lowest excited state is 1.42 eV, at the SCF level. This quantity is a lower limit, since the excited state, having an electron in a diffuse orbital, should be less stabilized than the ground state when correlation is introduced. The energy gap rises to 1.83 eV after completion of the extensive CI described above, and 1.87 eV after Davidson's correction.

C. Radical. This neutral electronic state is obtained from the previous one by removing the electron from orbital $11a'$. Both the orbital shapes and the equilibrium geometry of the radical closely resemble that of the lowest anion excited state, which is not surprising since a loosely bound electron in $11a'$ is not expected to influence significantly the other electrons and the nuclei. Thus, the unpaired electron remains largely on the CH₂ group rather than being extensively delocalized. A quantity of considerable interest is the dipole moment of this state, since it could be responsible for the stability of the excited anion. Its calculated value with the DZ basis set is 3.70 D at the SCF level, which is sufficient[30] for qualitative reliability since the dipole moment is a one-electron property. To be sure, we recalculated in the (DZ + P) basis set, which lowered the previous value somewhat to 3.54 D.

Discussion

Without correction (Davidson's or zero-point energy), our CI energy value for the excited anion and the experimental value for the radical match almost exactly: 1.83 eV above the ground-state energy. Our force field indicates that there will be no zero point energy correction from the a' vibrations, but a large negative correction is expected if some a'' vibrational frequencies are much smaller in the excited state than in the ground state. This is certainly the case for the CC torsional and CH₂ wagging frequencies, since the CC bond lengths are respectively 1.377 and 1.453 Å in the ground and excited states. From these bond lengths, one may roughly estimate[31] the CC torsional frequency to be 500 cm⁻¹ in the ground state, and 100 cm⁻¹ in the excited state. The CH₂ wagging mode frequency is expected to be comparable[32] to the torsional frequency, and to decrease in the same way upon CC lengthening. These estimated frequencies lead to the value –400 cm⁻¹, or –0.05 eV, for the zero-point energy correction. This roughly compensates for Davidson's correction (0.04 eV), indicating that the excited anion state may be very slightly bound, by 0.01 eV. Nevertheless, this value is much too small to be definitely conclusive, since it is generally considered that calcu-

(29) Mango, M. H.; Hoffmann, R. *J. Chem. Phys.* **1978**, *68*, 5498.

(30) Green, S. *Adv. Chem. Phys.* **1974**, *25*, 179. Green predicts an accuracy of 0.3 D for dipole moments calculated by a Hartree–Fock open-shell method, if there are no low-lying charge-transfer states.

(31) Further justification of our estimation of zero-point energy correction is based upon a normal mode analysis which will appear in a forthcoming paper.

(32) Herzberg, G. "Infrared and Raman of Polyatomic Molecules"; Van Nostrand: Princeton, N.J., 1945; p 326.

lations of the type described here are only accurate to ±0.15 eV.

Another argument supporting a bound excited anion state is our calculated value of the dipole moment of the radical. A recent discussion by Garrett[16b] suggests that such a large dipole moment must produce bound states. It is far above the critical dipole moment (1.625 D), and in the range (≥3.2 D) where nonionic polar molecules have been calculated by Jordan[9] to have positive electron affinities. In addition, the nodal nature of the 11a′ orbital, and similarities of the equilibrium geometries and the force-field matrices for the radical and the excited anion, suggest that the latter is well described as a radical binding a loose electron, thus strengthening the dipole argument. Finally, the optical transition from the anion ground state to this excited state is symmetry allowed, and suggests a substantial transition dipole moment. This is consistent with the experimental observation of a transition whose intensity is comparable to that associated with the photodetachment continuum cross section.

In conclusion, both the CI calculation on the anion and the calculated dipole moment of the neutral acetaldehyde enolate radical suggest that there is a Rydberg-like excited anion which may be bound. This state appears to be the most likely candidate to explain the resonances previously observed in electron photodetachment experiments.

The Nature of Hydrofluoric Acid. A Spectroscopic Study of the Proton-Transfer Complex $H_3O^+\cdot F^-$

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Abstract: Further spectroscopic measurements confirm the $H_3O^+\cdot F^-$ ion pair or proton-transfer complex as a predominant species in aqueous hydrofluoric acid. This complex owes its remarkable stability to a very strong hydrogen bond, mostly electrostatic. Being ionic, yet electrically neutral, it can account both for the essentially complete ionization of HF in water and the apparent weakness of the dilute acid. The ionization process may be represented by the double equilibrium $H_2O + HF \rightleftharpoons [H_3O^+\cdot F^-] \rightleftharpoons H_3O^+ + F^-$. The concentration of the various species cannot be determined from the spectroscopic data. However, the first equilibrium certainly lies well to the right, and cryoscopic data point to a value of about 15% for the dissociation of the complex. Dissociation can also occur in another way in the concentrated acid: $[H_3O^+\cdot F^-] + HF \rightleftharpoons H_3O^+ + HF_2^-$. Both the HF_2^- and separate H_3O^+ ions take part in the proton-migration process, which accounts for the sharp rise in conductivity with concentration. Deuterium fluoride is less strongly associated and less extensively ionized in solution than its hydrogen counterpart. Proton-transfer complexes with oxonium ions are also formed by anhydrous HF in various organic solvents.

Introduction

The surprising weakness of dilute hydrofluoric acid, in marked contrast with the three other hydrohalic acids,[1] has presented a challenge to the theory of chemical bonding. Conventionally the ionization of HF in water has been represented as a two-step process:

$$H_2O + HF \rightleftharpoons H_3O^+ + F^- \qquad (1)$$

and

$$HF + F^- \rightleftharpoons HF_2^- \qquad (2)$$
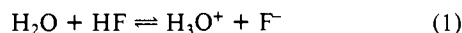
The first step, with an equilibrium constant in the range 2.4–7.2 × 10⁻⁴,[2] implies a dissociation of only a few percent. This unexpected behavior has been variously attributed to the greater strength of the H–F bond than that of the other hydrogen halides,[3] the hypothetical dimer H_2F_2,[4] or the equilibrium between chain structures of ions and ring structures of neutral HF molecules.[2] However, the very hypothesis of weak ionization is untenable, as explained elsewhere,[5] because it conflicts with a number of experimental facts. Foremost among those is the infrared absorption spectrum of aqueous hydrofluoric acid,[6] which shows great resemblance to that of the three other hydrogen halides, but also some differences. It is the analysis of that spectrum[7] which has led to the concept of hydrogen-bonded ion pair, or proton-transfer complex $H_3O^+\cdot F^-$.[8] Such a complex should have characteristic vibrations similar to, but distinguishable from, those of separate H_3O^+ ions. With this in view we have studied the vibrational spectra of (a) the concentrated acid as a function of temperature, (b) solutions of the bifluoride ion, HF_2^-, an important species in this system, and (c) the completely deuterated acid to confirm our assignments and detect any isotope effect.

Experimental Section

The spectra were recorded with the same equipment and much the same technique as in previous studies.[6,9] In infrared some difficulty was encountered in reproducing exactly the spectra of the saturated acid because of the high partial pressure of HF. However, these minor variations, mainly in the relative intensity of the 1840- and 1645-cm⁻¹ bands, do not affect significantly our interpretation of the results. The sample of deuterium fluoride prepared specially by Merck Sharp and Dohme (Montréal) was of high isotopic purity. The saturated solution contained only 38 mol% of DF in D_2O. (Unless otherwise stated concentrations are given throughout in mol%.)

(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Interscience, New York, 1966, p 223.

(2) H. H. Hyman and J. J. Katz in "Non-Aqueous Solvent Systems", T. C. Waddington, Ed., Academic Press, New York, 1965, Chapter 2, p 62.

(3) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

(4) R. P. Bell, "The Proton in Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1973.

(5) P. A. Giguère, *J. Chem. Educ.*, **56**, 571 (1979).

(6) P. A. Giguère and S. Turrell, *Can. J. Chem.*, **54**, 3477 (1976).

(7) P. A. Giguère, *Chem. Phys. Lett.*, **41**, 598 (1976).

(8) The name proton-transfer complex seems more appropriate here in view of the partial covalent character, as opposed to the purely Coulombic ion pairs of ordinary electrolytes. Likewise, the formula $H_3O^+\cdot F^-$ represents adequately the ionic, yet in effect neutral, character of the new entity.

(9) P. A. Giguère and C. Madec, *Chem. Phys. Lett.*, **37**, 569 (1976).