structure for the arsenic compound shows those carbon atoms to be most nearly saturated (as demonstrated by longer bonds to adjacent carbon atoms) that are most closely coordinated to the central arsenic atom.

We note finally that the more symmetric C_{2v} structures I and II show much less variation in C–C bond distances. For structures I and II the ranges of C–C distances are 0.11 and 0.09 Å, respectively, as compared to 0.20 Å for the lower energy structure III. This is of course consistent with the smaller range of P–C distances predicted for structures I and II.

Concluding Remarks

Complete theoretical structures have been predicted for four distinct conformers of the $P(C_5H_5)_2^+$ molecular ion. The theoretical energy differences suggest that separate identification of conformers of compounds of this class ought to be possible with techniques such as variable-temperature NMR. The lowest energy structure displays only a single plane of symmetry and is in some respects qualitatively similar to the crystal structure of As-$(C_5Me_5)_2^+$, reported in 1983 by Jutzi, Wippermann, Krüger, and Krauss.[15] The theoretical phosphorus structure, due in part to the absence of hindrance from methyl substituents on the Cp rings, is significantly more bent than the permethylated arsenic compound. Similarly, the phosphorus cation displays much more variation of the carbon–carbon bond distances within the Cp rings than does the arsenic structure. To the extent that Jutzi and co-workers are justified in labeling $As(C_5Me_5)_2^+$ as η^2 and η^3 with respect to the central arsenic atom, the lowest energy $P(C_5H_5)_2^+$

structure is best described as involving η and η^2 coordination. C–C distances in both rings are consistent with the electron distribution in the ring implied by these two types of interaction (P–C single bonding and three-center P–C$_2$ bonding, respectively); the same is true of the C–C distances and P–ring interactions in the three higher-energy conformations.

Since structure III of Figure 1 has the lowest energy for all levels of theory considered in this study, it is of interest to note that the HOMO (highest occupied molecular orbital) is an a″ orbital essentially concentrated in the lower ring and involving the $2p_x$ and $2p_y$ atomic orbitals (the xy plane is the plane of symmetry) of the 2′ and 3′ carbon atoms. The LUMO (lowest unoccupied molecular orbital), on the other hand, is an a″ orbital involving principally the phosphorus $3p_z$ orbital and the $2p_x$ and $2p_y$ atomic orbitals of the upper ring carbon atoms labeled by 2 in Figure 1. Apart from the phosphorus core orbitals (1s, 2s, and 2p), which are all very low lying, there are no MOs uniquely associated with phosphorus and hence no canonical MO which could be described as a phosphorus lone pair.

Does Fluoroformic Acid Exist?

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Abstract: This study was carried out for three reasons. The ab initio MO method is used for prediction of the existence of fluoroformic acid as an isolated species, arguments are given to explain the failure to synthesize this substance, and, finally, a previously reported potential energy surface for the van der Waals region of the $CFHO_2$ system is extended into the region of the bonded $CFHO_2$ molecule. The isolated fluoroformic acid molecule is found to be a stable species with a relatively high barrier for unimolecular decomposition into CO_2 and HF (210 kJ/mol), corresponding to a symmetry-forbidden-like reaction. In a protic medium fluoroformic acid decomposes with a low barrier, as indicated by the MNDO method. Cis and trans minima were found for the acid, as well as a saddle point for internal rotation. Infrared spectra were calculated for both conformers and vibrational analysis was performed for the transition states of internal rotation and dissociation processes.

Elementary textbooks of organic and inorganic chemistry generally state that the monofluoro derivative of carbonic acid does not exist because it decomposes immediately into CO_2 and HF (e.g., ref 1). The fluoride of carbonic acid, fluoroformic acid, FCOOH, is nevertheless mentioned in the literature. Attempts to isolate fluoroformic acid were usually carried out in aqueous solutions. Gordon and Lin[2] have studied the laser-induced reaction of :CHF + O_2. They proposed the formation of vibrationally excited fluoroformic acid and its unimolecular decomposition into CO_2 and vibrationally excited HF. They assumed a very low

activation energy for the unimolecular process in analogy to the observed activation energy of 54 kJ/mol for the related reaction, ClCOOH → HCl + CO_2, studied by Jensen and Pimentel.[3] However, the decay of chloroformic acid represents only one branch of a suggested mechanistic scheme of the radical photoreaction of chlorine with formic acid. Thus, the observed activation energy may not correspond to the monomolecular decomposition of chloroformic acid.

Cremer[4] has performed calculations for the ozonolysis of fluoroalkenes via the Criegee path.[5] He assumed the formation of fluoroformic acid during hydrolysis of the final ozonide and calculated the energy of fluoroformic acid at its standard geometry

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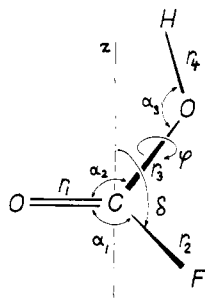(5) Criegee, R. *Angew. Chem.* **1975**, *87*, 765.

Figure 1. Definition of the internal coordinate set for fluoroformic acid. Atoms O=C—O define the *xy* plane.

at the 4-31G and 6-31G* + MP2 levels. The calculated heat of formation was $\Delta H_f^\circ{}_0$ = -586 kJ/mol at the 4-31G and -593 kJ/mol at the 6-31G* + MP2 levels. However, the recent experimental paper by Agopovich and Gillies[6] on the mechanism of ozonolysis of fluoroethylenes did not mention the possible formation of fluoroformic acid.

In addition to Cremer's paper, two other theoretical studies deal with fluoroformic acid. Takahashi[7] calculated the electronic properties of fluoroformic acid by the Hückel MO method. Ditchfield, Del Bene, and Pople[8] calculated n–π* transition of hypothetical fluoroformic acid. No discussion of the stability of fluoroformic acid has been given.

Although the identification of fluoroformic acid has not yet been reported, esters (see, e.g., ref 9), anhydrides,[10] and a salt[11] of fluoroformic acid have been isolated. McMahon and Northcott[11] have studied the anion of fluoroformic acid and estimated the heat of formation of the corresponding acid, $\Delta H_f^\circ{}_{298}$ = -640 kJ/mol.

Some other minima can be found on the $CFHO_2$ potential energy surface (PES), on which fluoroformic acid lies. Carbonyl oxide formation is assumed in the ozonolysis mechanism and fluorocarbonyl oxide is isomeric with fluoroformic acid. This system had been studied theoretically by Cremer.[4] He identified this structure as a transition state (saddle point on the PES) with rather high energy. Some other metastable structures that could be located on the $CFHO_2$ PES can be imagined: a family of carbenes, :C(OH)(OF), :CF(OOH), and :CH(OOF), and, for example, $CH(=O)(OF)$.

There also exists a van der Waals (vdW) chemistry of the $HF\cdots CO_2$ system. Hobza, Hofmann, and Zahradník[12] found a linear minimum of $O=C=O\cdots H—F$ type (see also ref 25), which was experimentally confirmed by Klemperer et al.[13] They also found a planar transition state with contact between the C and F atoms. It is clear that the vdW PES has not yet been completely described. There must be at least one minimum separating the symmetry-related saddle points.

This paper is concerned with that part of the potential energy surface of the $CHFO_2$ system which corresponds to fluoroformic acid and to its decomposition. The first section will deal with the structure and vibrational spectra of the cis and trans conformers of fluoroformic acid and with the interconversion of these forms. The second section will consider the unimolecular decomposition of fluoroformic acid into its components. A reason will also be given for the failure to isolate fluoroformic acid.

Computational Details

1. Search for PES Minima. The cis (φ = 0°) and trans (φ = 180°) minima (Figure 1) of fluoroformic acid were optimized at the ab initio 3-21G level[14] with use of the Newton-Raphson

optimization scheme.[15] The energy gradients in Cartesian coordinates were calculated by the HONDO 5 program[16] and transformed into a set of internal coordinates by using the chain rule. The internal coordinates are defined in Figure 1. The elements of the Hessian, the second derivatives of the energy with respect to internal coordinates, were evaluated by differentiation of the internal coordinate gradients. The differences in the internal coordinates for calculation of the Hessian were taken as 5.29 × 10^{-11} m (0.01 bohr) for the bond distances and 0.01 rad for all angles. The final Hessian was symmetrized. The Hessian evaluated for the starting geometry was retained in all the steps of the optimization process, and the optimization was stopped if any element of energy gradient was smaller than 0.001 hartree/bohr or hartree/rad.

2. Search for the PES Saddle Points. This was started at the trans minimum and used the method described by Cerjan and Miller,[17b] which is related to the Pancíř procedure,[17a] for walking uphill. The starting direction was chosen to follow the first as well as the second eigenvector of the Hessian. The first out-of-plane path led directly to the rotational transition state, the saddle separating the cis and trans minima. The second path also started with an out-of-plane motion and then switched into the same path leading to the rotational saddle point. The Hessian was not evaluated in each step, as suggested by Cerjan and Miller.[17b] The energy calculated directly by the HONDO 5 program for shifted coordinates was compared with the energy of the same point based on the quadratic approximation,

$$E^{i+1} = E^i + \bar{g}^i \Delta \bar{x} + \frac{1}{2} \Delta \bar{x} H^i \Delta \bar{x} \qquad (1)$$

where E^i, $\bar{g}^i$, and H^i are the energy, gradient, and Hessian at the previous point i, E^{i+1} is the energy at the new point, and $\Delta \bar{x}$ is the vector of the shift in the internal coordinates between the previous and the new points. Provided the differene in the calculated and expected changes in the energy was less than 10% of the calculated energy change, the Hessian was not updated and only the new gradient was evaluated. For the whole walk-uphill path only three Hessian evaluations were necessary, although the whole path has 13 steps.

We were not able to find a saddle point for the dissociation reaction FCOOH → CO_2 + FH, using the procedure of Cerjan and Miller.[17b] We have found that the walk-uphill procedures are useful in the search for the lowest saddle point around a specific minimum. Such a saddle point is not necessarily chemically important. For many chemical systems a set of internal rotations and inversions can be found rather than a saddle point corresponding to the chemical reaction.

To find the dissociation transition state, a combined method was chosen. First, we started with an estimated geometry in which the H–F distance was assumed to be 0.12 nm and the C–F and O–H distances were assumed to be longer by 0.02 nm than at the trans minimum. The saddle point was located by the MNDO method[18] by using the Cerjan–Miller search procedure employing the QCPE program[19] modified in our laboratory. The MNDO saddle point was used as a starting point for the 3-21G calculations. Because we were already in the descent region (one eigenvalue of the Hessian at the starting point and the λ parameter of the Cerjan–Miller procedure were negative), the Newton–Raphson method for searching was used (in the descent region this is identical with the Cerjan–Miller procedure). The Hessian was computed only once in the starting structure of the MNDO saddle point. Three gradient evaluations led to the optimized structure of the saddle point.

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Table I. Structural Parameters and Energy of the Cis and Trans Minima of Fluoroformic Acid and of the Rotational Transition State and Transition State of the Reaction FCOOH → CO_2 + HF, Calculated at the Ab Initio and MNDO Levels[a]

method	r_1(C=O)	r_2(C—F)	r_3(C—O)	r_4(O—H)	α_1(O=CF)	α_2(O=CO)	α_3(COH)	δ(CF,z)	φ(O=COH)	energy/heat of formation
cis-Fluoroformic Acid										
3-21G	0.1185	0.1328	0.1331	0.0977	123.5	127.8	112.6	90.0	0.0	−286.031320
6-31G										−287.493848
6-31G**										−287.635008
MNDO	0.1226	0.1315	0.1350	0.0950	111.1	126.2	114.2	90.0	0.0	−599.346
trans-Fluoroformic Acid										
3-21G	0.1175	0.1351	0.1330	0.0976	122.8	127.3	114.4	90.0	180.0	−286.028128
6-31G										−287.491110
6-31G**										−287.630863
MNDO	0.1221	0.1325	0.1348	0.0950	122.1	122.9	116.1	90.0	180.0	−593.353
Rotational Transition State										
3-21G	0.1179	0.1341	0.1346	0.0979	121.8	127.6	116.1	91.6	91.8	−286.016672
6-31G										−287.480526
6-31G**										−287.618155
MNDO	0.1220	0.1321	0.1359	0.0950	122.0	124.7	113.9	94.3	101.6	−580.380
Transition State of the Reaction FCOOH → CO_2 + HF										
3-21G	0.1146	0.1730	0.1253	0.1180	119.1	153.6	87.8	90.0	180.0	−285.954214
6-31G										−287.409819
6-31G**										−287.551753
MNDO	0.1204	0.1477	0.1284	0.1398	120.3	146.9	83.1	90.0	180.0	−230.299

[a] Bond distances are in nm, angles in deg, energy from the ab initio calculations in hartrees, heat of formation calculated at the MNDO level in kJ/mol.

3. Calculations of Vibrational Spectra.

Vibrational frequencies were calculated by using a standard FG analysis.[21]

The vibrational intensities were calculated by using the expression given by Blom et al.[22] The derivatives of the dipole moment with respect to internal coordinates were evaluated numerically and they were then transformed into the derivatives with respect to normal coordinates.

Structure and Properties of Fluoroformic Acid

Two local minima have been found for fluoroformic acid on the ab initio 3-21G as well as semiempirical MNDO levels. The minimum with the hydrogen atom oriented towards the carbonyl group is called cis. The second minimum, with the hydrogen atom oriented toward the fluorine atom, is called trans. The energies of the two minima have been recalculated at the 6-31G and 6-31G** levels[23] for the structure of the 3-21G minima. The structural parameters and energies are summarized in Table I. The two minima are separated by a low barrier, also described in detail in Table I. The cis conformer was found to be by 8.4, 7.1, and 10.9 kJ/mol more stable than the trans isomer according to 3-21G, 6-31G, and 6-31G** calculations, respectively. The MNDO method yielded comparable results; the cis conformer is more stable by 5.9 kJ/mol. Comparison of the energy of fluoroformic acid with the sum of energies of its components, CO_2 and HF, calculated in the 3-21G minimum, indicates that the cis conformer is more stable by 32.2 kJ/mol; however, it is less stable by 7.1 and 18.0 kJ/mol if the energy is recalculated at the 6-31G and 6-31G** levels, respectively. The MP2/6-31G**//HF/3-21G level predicts that the cis conformer of fluoroformic acid is less stable by 30.0 kJ/mol. The MNDO method predicts that the cis form of fluoroformic acid is more stable than the components by 8.1 kJ/mol. This is comparable with the 3-21G calculation. Moreover, the heat of formation of fluoroformic acid calculated by the MNDO method agrees very well with the estimate based on protonation of the anion of fluoroformic acid.[11] The rotational saddle point is higher by 38.1, 35.2, and 44.4 kJ/mol than the 3-21G, 6-31G, and 6-31G** cis minimum, respectively. Because the rotational transition state was optimized with respect to all degrees of freedom, it is interesting that none of the bond distances,

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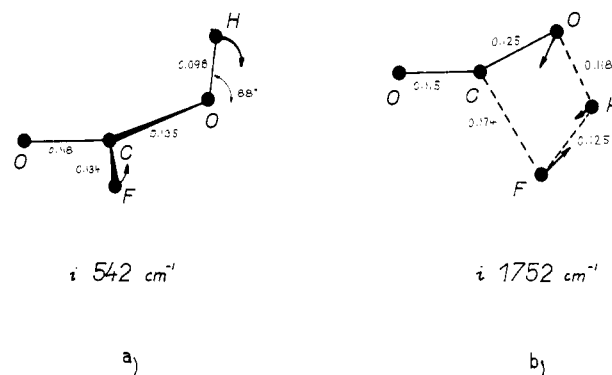
Figure 2. Transition vectors for the rotational (a) and decomposition (b) transition states calculated at the 3-21G level.

bond angles, and the dihedral angle are affected much on going from the minimum to the saddle point. A simplified description of a rigid rotor model is appropriate for this type of motion. The MNDO rotational transition state is slightly different from the ab initio one and differs from ideal bisected geometry for the H atom by 12 degrees (2 degrees for 3-21G). The dihedral angle φ is, as usual, oriented towards the higher-lying trans minimum for the saddle point located by the two methods. Vibrational analysis was carried out on the rotational transition state at the 3-21G level. The transition vector corresponding to the imaginary frequency is depicted in Figure 2.

Unimolecular Decomposition of Fluoroformic Acid

Fluoroformic acid has not been isolated yet. Is decay into its components an intrinsic property of this molecule? To answer this question, we looked for low-lying transition states surrounding the fluoroformic acid minima. In addition to the rotational transition state, we have found a transition state corresponding to the reaction FCOOH → CO_2 + HF. The structural parameters and energy of this transition state are given in Table I. The activation energy of the dissociation transition state is 194, 213, and 208 kJ/mol (calculated for the trans minimum of fluoroformic acid), as given by the 3-21G, 6-31G, and 6-31G** calculations, respectively. The zero-point energy correction reduces this value by 8.4 kJ/mol. The MNDO calculations yield a higher activation energy of 363 kJ/mol. The transition state represents a four-center, four-electron system. A reaction with such a transition state with an ideal square geometry is a symmetry-forbidden

Figure 3. The reaction profile for the reaction $FCOOH + H^+ \rightarrow CO_2$ $+ HF + H^+$. (Distances are in nm, angles in deg, enthalpy in kcal/mol.)

Figure 4. IR spectrum of the cis conformer of fluoroformic acid.

Figure 5. IR spectrum of the trans conformer of fluoroformic acid.

Figure 6. The reaction profile for interconversion of the conformers of fluoroformic acid and for decay of the trans form into its components.

process. The height of the barrier for the decomposition of fluoroformic acid can be interpreted in terms of the nature of the transition state; the unimolecular decomposition is characterized as a symmetry-forbidden-like process. A similar transition state has been found for the reaction of carbon dioxide with water by Jönsson et al.[24] The energy barrier of 224 kJ/mol for the reaction $H_2CO_3 \rightarrow H_2O + CO_2$ has been found at the CI level. This is much higher than the experimentally determined barrier, 74 kJ/mol. The authors explained the differences in the results by the possible interaction of the transition states of carbonic acid with an additional water molecule to avoid the high monomolecular barrier. We suppose that a similar process can play a role during the decomposition of fluoroformic acid. Isolated fluoroformic acid should be stable as the barrier for its decomposition is rather high. In a protic solvent, however, this molecule undergoes a reaction catalyzed by a proton, $FCOOH + H^+ \rightarrow HF + CO_2 + H^+$, with a low-energy barrier. We have found the transition state for this reaction at the MNDO level. The energy profile for the catalytic decay of fluoroformic acid and the transition state are depicted in Figure 3.

Conclusions

We have optimized all structures at the 3-21G level (or, for comparison, at the MNDO level) and recalculated the energy for this geometry using a larger basis set, including polarization functions. The results were qualitatively identical. There are a number of sources of possible error in this study. The limited accuracy of ab initio methods is well-known.

Fluoroformic acid was found to be separated from its components, CO_2 and HF, by a relatively high barrier (about 210 kJ/mol). It means that the acid is kinetically stable. Its thermodynamic instability relative to free components predicted by the MP2 calculations (30 kJ/mol) has no serious influence on this conclusion.

Fluoroformic acid should exist either as an isolated molecule, for example, in cosmic space, or in a nonprotic medium, where the concentration of protons able to catalyze its decomposition is negligible. The concentration of fluoroformic acid in the nonprotic medium must be very low, to avoid autocatalytic decay in which another molecule of fluoroformic acid is the source of a proton. Probably the best approach is to trap the molecules of fluoroformic acid in a matrix.

An attempt has been made here to predict the stability of an unknown species. Additional information is provided for the experimentalist: we have calculated the infrared spectra for both the cis and trans conformers of fluoroformic acid. It is known that the IR frequencies calculated at the ab initio SCF level are overestimated by about 10%; however, the spectra can help with identification of fluoroformic acid. The spectra are depicted in Figures 4 and 5. Figure 6 gives the reaction profile for the interconversion of the cis and trans forms of fluoroformic acid and its decomposition into CO_2 and HF. We assumed that the hydrogen-bonded van der Waals complex found by Hobza et al.[12] lies on the decomposition path.

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