tensively as necessary to reach (in principle) any desired degree of search convergence. With the current objective, the high symmetry of cycloheptadecane reduces the number of possible conformers substantially. Consequently, the continuous process searches take advantage of the fact that the cycloheptadecane conformational searches converge (cease to find new, distinct conformers) sooner than they would if the molecule being analyzed was less symmetrical. Systematic search methods like the tree-search methods described above make it difficult to take advantage of all symmetry elements and tend to approach all conformational problems as if they were the more complex (but more general) unsymmetrical ones.

We believe that we have found most if not all of the conformers within 3 kcal/mol of the global minimum. Among these low-energy conformers are a significant number having high energy substructures such as +g/−g pentane segments and nearly eclipsed C–C bonds. In defining the set of low-energy conformers, we have taken care to be sure that all structures found by the searches and subsequent energy minimizations represent true minima. The best way to verify structures as true minima was to reminimize structures by using the full-matrix Newton–Raphson technique to gradients <0.001 kcal/Å-mol and then examine the vibrational frequencies for imaginary modes. Without such a test, it was not possible to distinguish true minima from saddle point structures or unconverged geometries lying in relatively flat areas of the MM2 potential energy surface.

In conclusion, the cycloheptadecane problem, even though simplified by symmetry, appears to be a challenging but solvable problem in conformational analysis. It has served here as a test for several newly developed techniques for searching conformational space. Since this 17-membered ring lies just at the limit of what can be accomplished in a reasonable length of time, it should provide a good test of the effectiveness of new methods as they are developed.[20]

Registry No. Cycloheptadecane, 295-97-6.

Supplementary Material Available: A listing of all conformations found within 3 kcal/mol of the ground state giving MM2 energies and torsion angles and stereopair plots of all conformers within 1.0 kcal/mol of the global minimum (11 pages). Ordering information is given on any current masthead page.

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Empirical and ab Initio Estimates of the Stabilities of Fluorine-Containing Cations[1]

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Abstract: Heats of formation of two classes of monofluorinated cations, fluoronium ions and α-fluoro carbocations, are estimated ab initio and empirically. $C_3H_6F^+$ structures that are isoelectronic to stable C_3H_6O isomers are examined on the SCF potential energy surface (6-31G** basis set). The cations isoelectronic to alcohols all correspond to ion–molecule complexes between $C_3H_5^+$ and hydrogen fluoride where the equilibrium C–F bond distances are calculated to be >2 Å. The cation isoelectronic to propylene oxide is predicted to be unstable with respect to 1-fluoroisopropyl structures with planar skeletons. The remaining cations resemble their isoelectronic neutrals. Empirical estimates are based on core-ionization energies by using the method of equivalent cores. The two methods provide estimates within 15 kJ mol^{-1} (= 3.6 Kcal mol^{-1} = 0.16 eV) of each other in a number of cases so long as appropriate isodesmic reactions are used. For nonisodesmic reactions equivalent-cores approximations can be substantially in error. The agreement between equivalent cores and ab initio estimates are evaluated for the two isodesmic reactions $R_1OR_2 + (CH_3)_2F^+ \rightarrow R_1FR_2^+ + (CH_3)_2O$ for fluoronium ions and $O{=}CXY + CH_3CHF^+ \rightarrow FCXY^+ + CH_3CHO$ for α-fluoro carbocations. The SCF electronic energy changes, ΔE_1, when the ions are constrained to the geometries of their isoelectronic neutrals are found, in most cases, to agree with experimental values. By using correlations based on ΔE_1, core-ionization energies for oxygen-containing molecules are predicted: 539.4 eV for acetone enol, >539.5 eV for the lowest triplet state of acetone, and 538.9 eV for formamide with the nitrogen lone pair twisted out of conjugation with the carbonyl. ΔH_f values computed for ions in their relaxed geometries agree, for the most part, with equivalent cores estimates. Substituent effects are evaluated ab initio by computing the energy barrier for rotation about the C=N bond of $RCH{=}NH_2^+$: SCF values of $\Delta H^\ddagger$ for R = H, F, and vinyl at 6-31G** are 261, 190, and 166 kJ mol^{-1}, respectively. For cyclic fluoronium ions, the four-member ring ion fluoretanium is estimated to have ΔH_f = 660 kJ mol^{-1}, within 10 kJ mol^{-1} of two other $C_3H_6F^+$ isomers, $FCH_2CHCH_3^+$ (**14**) and $CH_3CH_2CHF^+$ (**2**). The five-member ring fluorolanium and the six-member ring fluoranium are estimated to have heats of formation of 555 and 515 kJ mol^{-1}, respectively.

Although fluorine is the most electronegative element, the consequences of substituting a cation with fluorine are not obvious. In recent years we have described gas-phase chemistry of the 2-fluoroisopropyl cation, **1**, which can be easily formed.[2,3] When it has sufficient internal energy **1** expels hydrogen fluoride in a simple 1,2-elimination without undergoing any rearrangement. This raises the question as to whether **1** might represent the only

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[†] University of California.
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[1] Portions of this work were presented at the 194th National meeting of the American Chemical Society, Los Angeles, CA, September 1988.

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minimum on the $C_3H_6F^+$ potential energy surface that is thermodynamically stable with respect to elimination. Since experimental data are not available, we resort to methods of estimation. This paper applies two approaches to a variety of simple monofluorinated cations.

The availability of heats of formation for gaseous cations has had a substantial impact upon the ability of mechanistic chemists to predict and analyze reaction pathways. When $\Delta H_f°$ has not been experimentally measured, there are at least two ways to obtain a useful estimate. One is through the use of molecular orbital calculations. The other is an empirical approach called the method of equivalent cores, which was introduced by Jolly and co-workers.[7] This paper will discuss these techniques as applied to organic molecules containing a single oxygen atom and their isoelectronic fluorinated ions.

$$\begin{array}{lcccc} & (CH_3)_2C{=}O + & CH_3CHF^+ \rightarrow & (CH_3)_2CF^+ + & CH_3CHO \quad (1) \\ \Delta H_f\ (kJ/mol) & -217 \pm 1^{4} & 696 \pm 4^{5,6} & 577 \pm 7^{6} & -166 \pm 0.5^{4} \end{array}$$

Equivalent-cores estimates can be compared with experimentally determined heats of formation. For monofluorinated, even-electron ions with at least two carbon atoms there are four cations for which reliable heats of formation have been reported: 1-fluoroethyl cation[5] (isoelectronic with acetaldehyde), 2-fluoroisopropyl cation[6] (**1**, isoelectronic with acetone), 1-fluorovinyl cation[8] (isoelectronic with ketene), and dimethylfluoronium[9] (isoelectronic with dimethyl ether). A comparison among these shows that the method of equivalent cores is accurate within ±15 kJ mol^{-1} when it is applied to isodesmic processes.

$$(CH_3)_2CO + CH_3CHO^{•+}(1s) \rightarrow (CH_3)_2CO^{•+}(1s) + CH_3CHO \quad (2)$$

The metathesis shown in eq 1 is a hypothetical reaction representing an isodesmic process, in which "the numbers of bonds of each formal type are conserved, and only the relationships among the bonds are altered".[12] The method of equivalent cores equates ΔH of eq 1 to the difference in oxygen 1s core ionization energies represented in eq 2. The O_{1s} core-ionization energy of acetone is reported to be 0.66 eV lower than that of acetaldehyde.[11] The measured core-ionization energies therefore give an energy change for eq 2 of $\Delta E_{EC} = -64$ kJ mol^{-1}. The value for ΔH for eq 1, based on the experimental gas-phase heats of formation of the reactants and products, is -68 kJ mol^{-1}, with an experimental uncertainty of ±8 kJ mol^{-1}. (The experimental uncertainty in measuring core-ionization energies is, at best, ±0.03 eV, so the aggregate uncertainty in the comparison is on the order of 10 kJ mol^{-1}).

Table I. Typical Examples of Fluorine-Containing Cations and Their Isoelectronic Oxygen Analogues and Corresponding Oxygen Core Ionization Energies in eV[j]

fluorinated ion	$\Delta H_f°$	oxygen analogue	$\Delta H_f°$	O_{1s} I.E.
1, $(CH_3)_2CF^+$	580[6]	$(CH_3)_2CO$	−217	537.98[11]
2, $CH_3CH_2CHF^+$	655[a]	CH_3CH_2CHO	−186	538.50[11]
3, $(CH_3)_2F^+$	605[9]	$(CH_3)_2O$	−184	538.59
4, $CH_2{=}CHFCH_3^+$	720[b]	$CH_2{=}CHOCH_3$	−107	539.01
5, CH_3OCHF^+	500[c]	$HCOOCH_3$	−356	538.45
6, $CH_3FCH{=}O^+$	570[d]	$HCOOCH_3$	−356	539.88
7, $CH_3OCFCH_3^+$	390[e]	CH_3COOCH_3	−412	537.92
8, $CH_3FCOCH_3^+$	470[f]	CH_3COOCH_3	−412	539.46
9, $H_2C{=}CHCHF^+$	745[g]	$H_2C{=}CHCHO$	−68[13]	538.17
10, H_2NCHF^+	585,[h] 580[i]	$HCONH_2$	−186[14]	537.74
11, $H_2C{=}CF^+$	950[8]	$H_2C{=}C{=}O$	−48	540.25

[a] Using **1** + $CH_3CH_2CHO \rightarrow$ **2** + $(CH_3)_2CO$. [b] Using **3** + $CH_2{=}CHOCH_3 \rightarrow$ **4** + $(CH_3)_2O$. [c] Using **1** + $HCOOCH_3 \rightarrow$ **5** + $(CH_3)_2O$. [d] Using **3** + $HCOOCH_3 \rightarrow$ **6** + $(CH_3)_2O$. [e] Using **1** + $CH_3COOCH_3 \rightarrow$ **7** + $(CH_3)_2CO$. [f] Using **3** + $CH_3COOCH_3 \rightarrow$ **8** + $(CH_3)_2O$. [g] Using **1** + $H_2C{=}CHCHO \rightarrow$ **9** + $(CH_3)_2CO$. [h] Using **1** + $HCONH_2 \rightarrow$ **10** + $(CH_3)_2CO$. [i] Using eq 9 with C_{1s} I.E.'s. [j] For fluorinated cations heats of formation are rounded off to the nearest 5 kJ mol^{-1} and, where indicated, were calculated by using the method of equivalent cores from the designated isodesmic reactions. Except where otherwise noted, calculated ΔH_f values are based on heats of formation for neutral molecules given in ref 4, group equivalents, and O_{1s} ionization energies from ref 10.

The method of equivalent cores assumes that on the scale of molecular dimensions there is little difference between an atom of atomic number Z with a vacancy in its 1s orbital (e.g., $O_{1s}^{•+}$) and a positive charge-bearing atom of atomic number $Z + 1$ (e.g., F^+). The heat of formation of a fluorine-containing cation should be equal to that of the core-ionized, isoelectronic oxygen-containing molecule minus a constant term. Core-ionization energies from the literature can be used to estimate the $\Delta H_f°$ values shown in Table I (several of the entries are updated from ref 7).

$$(CH_3)_2O + CH_3CHF^+ \rightarrow (CH_3)_2F^+ + CH_3CHO \quad (3)$$

Consider the metathesis shown in eq 3, which is not isodesmic. Since dimethyl ether and acetaldehyde have nearly the same O_{1s} core-ionization energy, equivalent cores would predict eq 3 to be nearly thermoneutral. The $\Delta H_f°$ values summarized in Table I show that the value of ΔH from experiment is -70 kJ mol^{-1}. There is clearly a discrepancy, which suggests that the method of equivalent cores may be accurate only when applied to isodesmic reactions.

Experimental and Calculational Methods

Core-ionization energies for gas-phase molecules were measured by using the Oregon State cylindrical mirror analyzer.[15] The experimental methods used to obtain these data and the analytical methods used to convert the experimental data to core-ionization energies have been previously described.[16] The results of these measurements are given in Table III.

Ab initio calculations were performed by using the GAUSSIAN 82 program (revision K)[17] on the CRAY X-MP/48 at the San Diego Supercomputer Center. Except where otherwise indicated, geometries were optimized by SCF calculations by using the 6-31G** basis set. Zero-point energy corrections of calculated energies are based on normal modes computations performed by using the 3-21G basis set on geometries optimized with that basis set (calculated vibrational frequencies were scaled down by a factor of 0.9 to correct for a systematic overestimate by Hartree-Fock methods[12]). Additional computations using ab initio wave functions were performed with NBO calculations by using an enhanced version of the Natural Bond-Orbital Wave Function Analysis

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Table II. Ab Initio Electronic Energies of Structures Used for Stability Estimates (SCF Optimized Geometries at 6-31G**)

	6-31G**	MP2[a]/6-31G**
CH_2O	−113.867 94	−114.188 92
CH_2F^+	−138.097 80	−138.389 62
HC≡CH	−76.821 84	−77.089 53
HC≡CF	−175.645 21	−176.077 31
$CH_2{=}CH_2$	−78.038 84	−78.326 84
$CH_2{=}CHF$	−176.887 57	−177.338 65
CH_3CHO	−152.922 59	−153.389 28
CH_3CHF^+	−177.182 18	−177.623 30
$(CH_3)_2O$	−154.074 11	−154.564 09
$(CH_3)_2F^+$	−178.341 55	−178.807 60
$CH_3CH_2CH_3$	−118.276 16	−118.740 79
$CH_3CHCH_3^+$	−117.393 75	−117.814 12
CH_3CHFCH_3	−217.130 27	−217.756 24
$(CH_3)_2CF^+$ (**1**)	−216.257 11	−216.847 03
$CH_3CF{=}CH_2$ (C_s symmetry)		
eclipsed[b]	−215.935 92	−216.536 14
staggered[b]	−215.931 79	

[a] Including core orbitals. [b] For definitions, see ref 22.

Program[18] in conjunction with the GAUSSIAN 86 program (revision C)[19] on a VAX 8700. Correlations between ab initio results and the method of equivalent cores were assessed by standard least-squares methods. Hole-state calculations were performed by using the MOLECULE-ALCHEMY program package, which incorporates the MOLECULE integrals program written by J. Almlof and the ALCHEMY program written by P. Bagus, B. Liu, M. Yoshimine, and A. D. McLean and modified by P. Bagus and U. Wahlgren.[20]

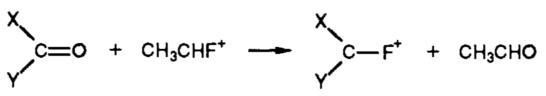
Results

The gas-phase basicity of $CH_3CF{=}CH_2$ has been measured by Szulejko and McMahon[21] as being very close to that of benzene. After making correction for entropy, we infer that the experimental ΔH for eq 4 is −763 ± 5 kJ mol^{-1}.

$$CH_3CF{=}CH_2 + H^+ \rightarrow (CH_3)_2CF^+ \qquad (4)$$

Ab initio computations using single-determinant wave functions do not give good agreement with this experimental value, as can be seen by considering results summarized in Table II. The change in electronic energy when 2-fluoropropene is protonated is −843 kJ mol^{-1}. When this is corrected for the change in zero-point energy, the computed value of ΔH for eq 4, −819 kJ mol^{-1}, is a substantial overestimate of the proton affinity of $CH_3CF{=}CH_2$. A post-SCF calculation (MP2) reduces the discrepancy with experiment, giving ΔH = −793 kJ/mol^{-1} after correction for zero-point energies.

Carbonyl Compounds and Their Isoelectronic Ions. Ab initio calculations often show better agreement with experiment when applied to isodesmic processes, such as eq 5. This is a generalized



(5)

case of eq 1 (for which the SCF electronic energy change, −67 kJ mol^{-1}, is within the uncertainty of the experimental value of ΔH and that of the equivalent-cores estimate). As noted above, equivalent cores agrees well with experimental values so long as isodesmic reactions are considered. We have performed hole-state calculations that confirm this agreement. If we consider eq 5 for formaldehyde (X = Y = H) and constrain geometries to the optimized structures of the neutral aldehydes, we can use the energy change to estimate the O_{1s} core ionization energy difference between formaldehyde and acetaldehyde (the method of equivalent cores in reverse). This predicts the O_{1s} core ionization energy for formaldehyde to be 0.70 eV higher than for acetaldehyde. The experimental value is 0.87 eV. Hole-state calculations on core-ionized formaldehyde and acetaldehyde at 6-31G** predict a core-ionization energy difference of 0.71 eV, which agrees with the equivalent cores estimate.

Now consider eq 3 and again use equivalent cores in reverse. For geometries frozen at the neutral molecule structures, we would suppose on the basis of SCF calculations that dimethyl ether ought to have a core ionization energy 0.23 eV lower than acetaldehyde. Hole-state calculations, on the other hand, predict that acetaldehyde should be lower than dimethyl ether by 0.08 eV, which is not far from the experimentally reported value of 0.03 eV. For this nonisodesmic reaction the hole-state calculations predict that the method of equivalent cores is in error by 0.31 eV. Of the 70 kJ mol^{-1} discrepancy between the equivalent-cores estimate for eq 3 and measured heats of formation, 30 kJ mol^{-1} can be ascribed to intrinsic errors associated with the equivalent cores approximation, while the remainder must be due to effects of geometric relaxation and changes in zero-point energy. These effects compensate in isodesmic reactions.

Consider estimates based on the isodesmic reactions in eq 5 and 6. SCF results for selected oxygen- and fluorine-containing molecules are summarized in Tables II–IV. Calculated geometries for carbonyl compounds agree well with the experimentally determined structures.[23] Table V compares equivalent-cores estimates with ab initio values for eq 5. Two different values are given for the electronic energy change: ΔE_1 is calculated assuming the geometry of the cation to be the same as that of the isoelectronic neutral; ΔE_2 is calculated by using equilibrium geometries for the cations. The SCF changes in electronic energy, ΔE_2, for eq 5 are (with the exception of **12**) within 20 kJ mol^{-1} of the empirical estimates by the method of equivalent cores. In most cases the changes in electronic energy when ionic structures are frozen at the carbonyl geometry, ΔE_1, do not greatly differ from the energy changes, ΔE_2, calculated when the ions are relaxed to their 6-31G** equilibrium geometries. Additional correction for changes in zero-point energies (based on 3-21G//3-21G normal modes calculations) does not produce ΔH values that differ substantially from ΔE_2. In other words, the assumption that the effects of geometric relaxation cancel appears to be largely validated in the case of eq 5.

Ethers and Their Isoelectronic Ions. Dialkyl fluoronium ions, $R_1FR_2^+$, can be expected to manifest substantial distortions relative to their isoelectric oxygen analogues. As we have previously

$$R_1OR_2 + (CH_3)_2F^+ \rightarrow R_1FR_2^+ + (CH_3)_2O \qquad (6)$$

discussed,[3] the two bonds to fluorine often have widely different heterolytic dissociation energies when $R_1 \neq R_2$. Only when $R_1 = R_2$ or when the two C–F bond strengths happen to be nearly the same should agreement between equivalent cores and ab initio estimates be anticipated.

Table VI summarizes results for eq 6. The standards for Tables V and VI (ΔE = 0 for acetaldehyde and ΔE = 0 for dimethyl ether, respectively) were chosen because these two compounds have oxygen core-ionization energies within 0.05 eV of one another. As predicted, ΔE_1 and ΔE_2 are within experimental uncertainty of ΔE_{EC} for oxetane (trimethylene oxide) and its isoelectronic fluoronium ion, fluoretanium. Both are calculated to have symmetrical, planar geometries (even though no such constraints were imposed upon the geometry optimization). As summarized in Table III, the O_{1s} ionization energies of tetrahydrofuran and tetrahydropyran are the same as for oxetane.

For methyl vinyl fluoronium, **4**, the values of ΔE_{EC} and ΔE_2 are in good agreement. In this case, the conformational minimum

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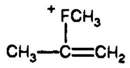
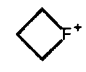
Table III. Experimental Core Ionization Energies and ab Initio Results (6-31G**//6-31G**) for Neutral Molecule[g]

	C_{1s} (eV)	O_{1s} (eV)	electronic energy (au)	bond lengths (Å)		bond angles (deg)	
1,3-butadiene	290.58[a]		−154.930 32	C=C	1.322	CCC	124.1
				C–C	1.467	HCH	116.7
acetyl chloride	291.97[b]	539.09[b]	−611.836 19	C–C	1.502	CCO	127.1
	295.39[b]			C=O	1.167	CCCl	112.9
				C–Cl	1.785	HCC[e]	110.4
oxetane	290.98	538.06	−191.918 82	C–C	1.536	CCC	83.9
	292.17			C–O	1.419	COC	92.8
propylene oxide[d]	290.98	538.44	−191.919 58	C–C	1.453	CCC	122.5
	292.31[a]			C–O	1.404	COC	62.3
2-methoxypropene	*a*	538.84[c]	−230.971 74	C=C	1.324	CCC	124.3
				C–O	1.348	C=CO	125.8
				C–C	1.499	COC	119.2
				O–CH_3	1.399	HCH[e]	117.1
tetrahydrofuran	290.75	538.09	*f*				
	291.94						
tetrahydropyran	290.58[a]	538.06	*f*				
	291.88						

[a] Includes more than one chemically nonequivalent carbon. [b] Siggel, M. R. F.; Carroll, T. X.; Thomas, T. D. Unpublished results. [c] Reference 31. [d] Nonplanar skeleton. Bond lengths given for atoms within the three-member ring. The two C–O bond lengths differ by less than 0.001 Å. The CH_3–C–C–O dihedral angle is calculated to be 103.5°. [e] Hydrogen(s) in the CCO plane. [f] Not calculated. [g] Except where otherwise noted, the carbon–oxygen skeleton is planar in the ab initio equilibrium geometries.

Table IV. Ab Initio Results for SCF Calculations (6-31G**//6-31G**) on Fluorine-Containing Cations[c]

ion		electronic energy (au)	bond lengths (Å)		bond angles (deg)	
$CH_3CH_2CHF^+$	**2**	−216.227 24	C–CCF	1.528	CCC	116.7
(*s*-cis)			CC–CF	1.448	CCF	121.7
			C–F	1.239	FCH	114.1
$CH_3FCH{=}CH_2^+$	**4**[a]	−216.180 48	C–FCC	1.538	CFC	123.1
			CF–CC	1.487	FCC	115.2
			C=C	1.296	FCH	107.2
$CH_2{=}CHCHF^+$	**9**	−215.054 26	C=C	1.357	CCC	117.0
(*s*-trans)			C–C	1.385	CCF	120.9
			C–F	1.256	FCH	114.4
$NH_2{=}CHF^+$	**10**	−193.240 46	N=C	1.265	NCF	119.8
			C–F	1.260	FCH	.17.0
$CH_2{=}CF^+$	**11**	−175.923 32	C=C	1.260	CCF	180
			C–F	1.203	HCH	121.8
CH_3CFCl^+	**12**	−636.082 62	C–C	1.468	CCF	117.5
			C–F	1.248	CCCl	126.1
			C–Cl	1.631	FCCl	116.4
 $CH_3-\overset{\overset{+}{F}CH_3}{\overset{\vert}{C}}{=}CH_2$	**13**[b]	−255.236 61	C–C	1.474	CCC	143.6
			C–FCH_3	1.594	C–C–F	106.6
			F–CH_3	1.493	C–F–C	125.3
$CH_3CHCH_2F^+$	**14**	−216.222 24	C–CCF	1.445	CCC	124.5
(*cis*)			CC–CF	1.464	CCF	112.0
			C–F	1.337		
	**18** (*n* = 1)	−216.207 57	C–F	1.554	CFC	88.8
			C–C	1.519	CCC	91.4

[a] Nonplanar geometry; C=C–F–CH_3 dihedral angle = 110.9° (a dihedral angle >90° means that the F-methyl in the skew structure is twisted away from the sp^2 carbons). [b] Nonplanar geometry; C=C–F–CH_3 dihedral angle = 96.3°. The C=C bond length is the same as for ion **4**. [c] Except where indicated, all the ions achieve planar geometries (although this was not imposed as a constraint of optimization).

Table V. Empirical (Method of Equivalent Cores) and ab Initio (6-31G**//6-31G**) Estimates of Energy Changes (in kJ mol^{-1}) for Eq 5[a]

				electronic	ab initio		
ion	X	X	ΔE_{EC}	energy (au)	ΔE_1	ΔE_2	ΔH
1	CH_3	CH_3	−64	−216.257 11	−58	−67	−68
2	CH_3CH_2	H	−14	−216.227 24	−13	−17	−16
9	$CH_2{=}CH$	H	−46	−215.054 26	−48	−66	−63
10	H_2N	H	−87	−193.240 46	−83	−106	−99
11	−CH_2−		+142	−175.923 32	+173	+171	+169
12	CH_3	Cl	+43	−636.082 62	+75	+34	+34

[a] Electronic energies (in atomic units) are given for the optimized geometries of the fluorine-containing ions. ΔE_1 designates the change in electronic energy calculated for ion structures frozen at the isoelectronic carbonyl equilibrium geometry. ΔE_2 designates the change in electronic energy calculated when all structures are allowed to relax to their equilibrium geometries. ΔH designates ΔE_2 corrected for zero-point energy differences computed from 3-21G normal modes calculations.

for methyl vinyl ether corresponds to a local maximum for ion **4**. The previously reported[3] planar structure of **4** is not the minimized geometry. The correct equilibrium geometry has the methyl–fluorine bond nearly perpendicular to the C=C–F plane. At 3-21G the planar *s*-trans and *s*-cis geometries have SCF electronic energies 3.9 and 5.9 kJ mol^{-1} higher. These differences are not so great as the *s*-cis (conformational minimum) minus *s*-trans (local maximum) energy for methyl vinyl ether at this calculational level, −14 kJ/mol.[24] With its skew geometry, **4** is chiral. The calculated SCF barrier for interconverting the two enantiomorphs via the lowest energy *s*-trans structure is 3.7 kJ mol^{-1} at 6-31G**. The zero-point energy correction (at 3-21G) is <0.1 kJ mol^{-1}.

In general, conformational energy differences for fluorine-containing ions are not as large as those of their isoelectronic neutral oxygen analogues. For example, the torsional potential

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[24] Bond, D.; Schleyer, P. v. R. *J. Org. Chem.* In press.

Table VI. Empirical (Method of Equivalent Cores) and ab Initio (6-31G**//6-31G**) Estimates of Energy Changes (in kJ mol^{-1}) for Eq 6[b]

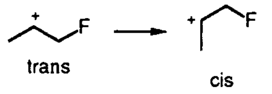
ion	R_1	R_2	ΔE_{EC}	electronic energy (au)	ab initio ΔE_1	ΔE_2	ΔH
4	CH_3	$CH_2{=}CH$	+38	−216.179 12	+53	+35	+23
13	CH_3	$CH_2{=}CCH_3$	+22	−255.236 61	+32	+7	−5
18 (*n* = 1)	$-CH_2CH_2CH_2-$		−53	−216.207 57	−61	−56	−61
14	$-CH(CH_3)CH_2-$		−16	−216.222 24[a]	−26	−93	−104
15	$CH_2{=}CHCH_2$	H	+16	−216.228 55[a]	+45	−79	−94

[a] The fluorine-containing ion lacks one of the covalent bonds that its isoelectronic oxygen analogue possesses. [b] Electronic energies (in atomic units) are given for the optimized geometries of the fluorine-containing ions. ΔE_1 designates the change in electronic energy calculated for ion structures frozen at the isoelectronic carbonyl equilibrium geometry. ΔE_2 designates the change in electronic energy calculated when all structures are allowed to relax to their equilibrium geometries. ΔH designates ΔE_2 corrected for zero-point energy differences computed from 3-21G normal modes calculations.

of ion **2** is qualitatively similar to that of propionaldehyde, for which the calculated energy difference between the two stable conformations is on the order of 5 kJ mol^{-1}.[25] In comparison, at 6-31G** we find that the *s*-cis geometry of **2** is only 1.9 kJ mol^{-1} more favorable than the other conformational minimum (where the corresponding CCCF dihedral angle is 94.3°).

In Table VI the ab initio values of ΔH differ from ΔE_2. In other words, zero-point energies for larger dialkylfluoronium ions are lower than would be expected based on the vibrational frequencies of ion **3**. We have previously remarked on this feature of unsymmetrically substituted fluoronium ions.[3] For the one symmetrical example in Table VI, fluoretanium, the SCF energy difference between ΔE_2 and ΔH is only 5 kJ mol^{-1}. For the unsymmetrical examples the difference is 12 kJ mol^{-1}.

The largest discrepancies are seen in cases where one of the bonds in the ion is much weaker than in the corresponding neutral. A fluoronium structure that is isoelectronic with propylene oxide was computed as being stable at the 3-21G level.[3] With the 6-31G** basis set, however, SCF calculations show that there is no barrier to its deformation to a 1-fluoroisopropyl cation structure in which the fluorine is nearly coplanar with the three carbons. This ion, **14** (to which the isoelectronic oxygen analogue is a zwitterion), is calculated to possess two stable conformers, cis and trans, depicted in eq 7. At 6-31G** the SCF energy of the trans state is 8 kJ mol^{-1} higher than that of the cis. From Table VI it can be seen that the calculated heat of formation of this cation is much lower than would be predicted from the core-ionization energy of propylene oxide.



(7)

14

Alcohols and Their Isoelectronic Ions. The method of equivalent cores overestimates the heat of formation of the fluoronium ion that is isoelectronic with allyl alcohol. The calculated minimum energy geometry is an ion–molecule complex of allyl carbon and hydrogen fluoride, **15**, whose structure is shown in Figure 1. This is isomeric with the [$CH_3C{=}CH_2^+$ FH] ion–molecule complex that we have previously described.[3] The minimal covalent character of **15** is illustrated by the low SCF energy barrier required to move hydrogen fluoride from one end to the other. The 6-31G**//6-31G** energy for the structure where the HF hovers over the central carbon (in which the complex is constrained to have a plane of symmetry) is only 10.8 kJ mol^{-1} higher than that of **15**.

$$(CH_3)_2CHFH^+ + ROH \rightarrow (CH_3)_2CHOH + RFH^+ \quad (8)$$

We note that ΔE_1 for allyl alcohol also disagrees with the equivalent cores estimate. (As previously noted, allyl alcohol possesses an *s*-cis geometry, both experimentally and ab initio.[26])

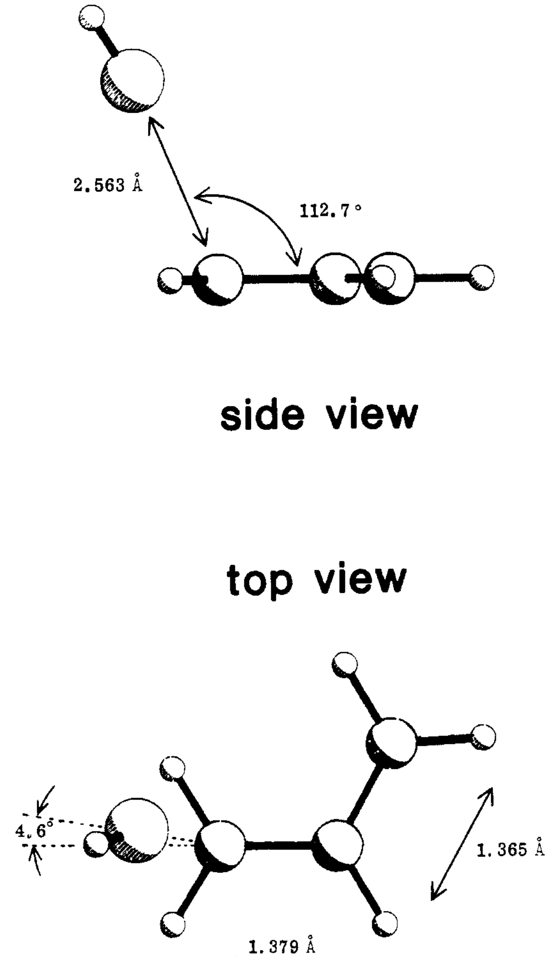
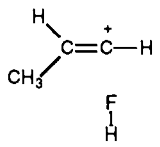
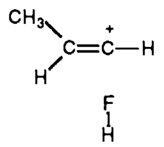


Figure 1.

For ab initio predictions of core ionization energies from equivalent cores, the isodesmic reaction in eq 8 should be used instead of eq 6. The SCF electronic energy change for eq 8 is ΔE_1 = 51 kJ mol^{-1} for R = methyl and 38 kJ mol^{-1} for R = allyl. The empirical estimates based on the method of equivalent cores are ΔE_{EC} = 60 and 26 kJ mol^{-1}, respectively.



(*Z*)-**16**



(*E*)-**16**

17

$E_{6\text{-}31G^{**}}$ −216.18472 −216.18404 −216.17698

There are three other isomeric C_3H_6O alcohols: the cis and trans enols of propionaldehyde and cyclopropanol. Geometry optimizations of the isoelectronic fluoronium ions shows that all three correspond to ion–molecule complexes, **16** and **17**, drawn

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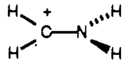
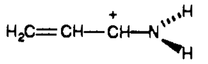
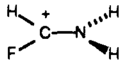
(25) (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 5817–5822. (b) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1988**, *9*, 488–494.

(26) (a) Vanhouteghem, F.; Pyckhat, W.; Van Alsenoy, C.; van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1986**, *140*, 33–48. (b) Kao, J.; Katz, T. *J. Mol. Struct.* **1984**, *108*, 229–239.

Table VII. Hartree–Fock Electronic Energies (in au), Heats of Formation (in kJ/mol), and Activation Barriers (in kJ/mol) to Rotation about the C–N Double Bond for Selected Iminium Ions[d]

cation	$E_{3\text{-}21G}$ (au)	$E_{6\text{-}31G^{**}}$ (au)	ΔH_f ($\Delta H^\ddagger$) emp	3-21G	6-31G**
$H_2C{=}NH_2^+$	−93.862 84	−94.394 72	745[a]	712[b]	745[b]
	−93.744 48	−94.288 41		(293)	(261)
$H_2C{=}CH\text{-}CH{=}NH_2^+$	−170.346 69	−171.312 04	774[c]	736	735
	−170.269 24	−171.244 29		(191)	(166)
$HCF{=}NH_2^+$	−192.173 47	−193.240 26	575[c]	578	562
	−192.089 39	−193.163 67		(209)	(190)

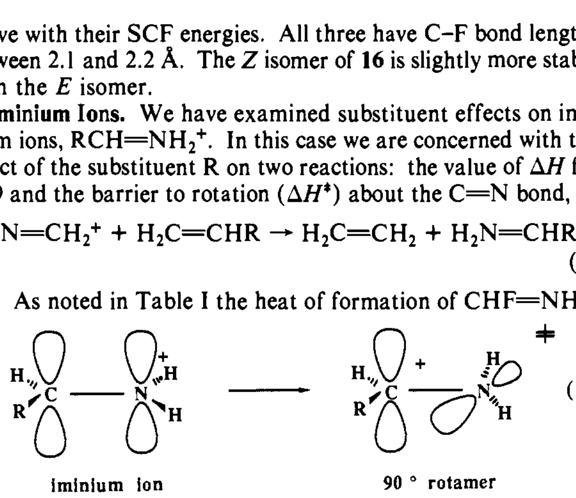
[a] Reference 27. [b] From eq 11. [c] From equation 9 using equivalent cores. [d] Empirical heats of formation estimated as indicated. Ab initio $\Delta H^\ddagger$ values for eq 10 (in parentheses) were determined from the electronic energies of the iminium ions and their 90° rotamers and zero-point energies ($3N$–6 normal modes for the iminium ions, $3N$–7 for their 90° rotamers).

above with their SCF energies. All three have C–F bond lengths between 2.1 and 2.2 Å. The *Z* isomer of **16** is slightly more stable than the *E* isomer.

Iminium Ions. We have examined substituent effects on iminium ions, $RCH{=}NH_2^+$. In this case we are concerned with the effect of the substituent R on two reactions: the value of ΔH for eq 9 and the barrier to rotation ($\Delta H^\ddagger$) about the C=N bond, eq

$$H_2N{=}CH_2^+ + H_2C{=}CHR \rightarrow H_2C{=}CH_2 + H_2N{=}CHR^+ \quad (9)$$

10. As noted in Table I the heat of formation of $CHF{=}NH_2^+$



(10)

can be estimated empirically in two ways, one based upon eq 5 using O_{1s} ionization energies and the other based on eq 9 using C_{1s} ionization energies. If we use the value 290.82 eV for the C_{1s} ionization energy of ethylene, the estimated heat of formation for $CHF{=}NH_2^+$ is only 5 kJ mol^{-1} lower than that estimated on the basis of eq 5. Table VII compares empirical and SCF estimates for R = F and R = H. As a calibration for the ab initio results we find that the empirical value of ΔH for the isodesmic reaction in eq 11 (using the published geometry of methylamine[12]) agrees with the computed electronic energy change. SCF calculation at 6-31G** gives a result, ΔH = 145 kJ mol^{-1}, that is within the uncertainty of the value based on experimental heats of formation.[27]

$$H_2C{=}NH_2^+ + CH_3CH_2CH_3 \rightarrow CH_3NH_2 + CH_3CHCH_3^+ \quad (11)$$

We compare R = fluorine and R = vinyl with R = H by examining their effects on the rotational barrier about the C=N bond of the substituted iminium ions. Since there are no empirical data for such an assessment, SCF calculations are used. The 90° rotamer geometries of the iminium ions were optimized with the sole constraint that the bisector of the HNH bond angle lies in the plane of the sp^2 carbon. Thus the NH_2 group was permitted to pyramidalize but not to rotate in this transition state. Normal modes analysis of the 90° rotamer was performed at 3-21G, and there is exactly one negative force constant, which corresponds to rotation about the C–N bond. The electronic energy change for eq 10 was converted to a $\Delta H^\ddagger$ by adding the zero-point energies of $3N$–6 degrees of freedom to the energy of the iminium ion and the zero-point energies of the $3N$–7 degrees of freedom with positive force constants to the energy of the 90° degree rotamer. (When we calibrate by performing the analogous 6-31G** calculation for formamide, we get an activation barrier of $\Delta H^\ddagger$ = 62 kJ mol^{-1} for rotation about the C–N bond, which agrees well with other ab initio values as well as the experimental result.[28]) Results of these calculations are given in Table VII.

We have considered only three iminium ions: R = H, vinyl, and F. As the entries in Table VII imply, the SCF estimates of ΔH based on eq 9 tend to be lower than the empirical estimates. If the iminium ions are constrained to the same geometries as their corresponding olefins, the 6-31G** electronic energy changes for eq 9 are −65 and +17 kJ/mol for R = vinyl and R = F, respectively, while the corresponding equivalent cores estimates are −29 and +21 kJ/mol. (The former is based upon the core-ionization energy of butadiene given in Table III). Estimated heats of formation in Table VII are based on optimized iminium geometries. The barrier to rotation about the C=N bond ($\Delta H^\ddagger$ for eq 10) is lowered substantially for both R = F and R = vinyl.

Discussion

Fully empirical estimates by equivalent cores and ab initio calculations of stabilities of transient cations can be compared. For instance, the three-member cyclic ion fluoriranium, shown eq 12, has been proposed as a short-lived intermediate in the gas phase.[29] An approximate ΔH_f° of this species can be calculated by applying the method of equivalent cores to the isodesmic reaction shown in eq 4, which equates ΔH to the difference in O_{1s} binding energies of oxirane versus dimethyl ether, ΔE_{EC} = 24 kJ/mol.[10] Published ab initio computations of the change in electronic energy give 17 kJ/mol at the SCF level (6-31G*//6-31G*) and 24 kJ/mol after a post-SCF (MP2) calculation.[30]

(12)

In the present work SCF calculations on isodesmic reactions involving ions agree, for the most part, with empirical estimates based on the method of equivalent cores. The comparison between ΔE_{EC} and ΔE_1 in Tables V and VI is appropriate, for this comparison is independent of the effects of geometrical relaxation. Of 11 entries in these tables, eight show agreement within ±15 kJ mol^{-1}. It seems unlikely that a fortuitous cancellation of errors occurs in the comparison of empirical with ab initio results. The systematic errors in the former arise from equating F$^+$ with a core-ionized oxygen atom. The systematic errors in the latter arise from the use of single-determinant wave functions and limited basis sets to represent them. SCF calculations overemphasize the role of charge-separated resonance structures, and we have argued that this renders them peculiarly suitable to evaluate the energies

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(27) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1.

(28) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935–5943.

(29) Ciommer, B.; Schwarz, H. *Z. Naturforsch.* **1983**, *38B*, 635–638.

(30) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810.

of isodesmic reactions involving positive ions.[3] For fluorine-containing cations, the weight given to heterolytic hyperconjugative structures is not so excessive as it is for uncharged molecules. Provided that errors cancel for the neutral reaction partners in an isodesmic reaction, we expect that the extent to which SCF and empirical values for ΔE_1 agree provides a calibration of the Hartree–Fock model for the ions.

The method of equivalent cores predicts a linear relationship between experimental core ionization energies and ΔE_1. Since the reference molecules in eq 5, 6, and 8 all happen to have ionization energies that are close to one another (538.64 eV for acetaldehyde,[9] 538.59 eV for dimethyl ether,[10] and 538.51 eV for isopropyl alcohol[31]), a single expression can be used for carbonyl oxygen, ethers, and alcohols. The relation IE = 538.57 eV + 24.1 ΔE_1 (ΔE_1 in atomic units) fits the experimental data for all 15 compounds with a correlation coefficient $r = 0.99$. Since ΔE_1 values are based on identical geometries for isoelectronic molecules, the extent to which the slope (which has a standard deviation of 1.0) differs from the number of eV in an atomic unit (27.2) is a measure of the agreement between our SCF calculations and the method of equivalent cores independent of any effects from geometrical relaxation.

By using this correlation and the calculated value of ΔE_1 for acetone enol in eq 8 we predict that the O_{1s} ionization energy of acetone enol should be 539.39 eV, in agreement with a previously reported estimate.[31] We can also estimate core-ionization energies for species that correspond to transition states, such as 90°-twisted formamide: the value of ΔE_1 for eq 5, +39 kJ mol^{-1}, predicts a core-ionization energy of 538.93 eV. Finally, this relationship predicts that the O_{1s} ionization energy of acetone in its first excited state should be substantially higher than that of acetone. Ab initio calculations[3] show that the triplet energy of ion **1** is at least 1.9 eV greater than that of acetone. ΔE_1 will be shifted accordingly, and the mean O_{1s} ionization energy of triplet acetone should be ≥ 1.9 (24.1/27.2) eV above that of acetone (in other words, >539.65 eV).

For ethers the discrepancies between ΔE_{EC} and ΔE_1 in Table VI are all ≤15 kJ/mol. For allyl alcohol, the discrepancy in Table VI is on the order of 30 kJ/mol, which suggests that the method of equivalent cores is not transferable between ethers and alcohols. We therefore introduce eq 8 for relating ΔE_1 to ΔE_{EC}. For estimates of $\Delta H_f°$ for RFH^+, methanol (whose core ionization energy is 539.13 eV[10]) should be used as the reference compound in eq 8 instead of isopropyl alcohol, since the proton affinity and heat of formation of fluoromethane are known.[9] (Protonated 2-fluoropropane has never been reported, and ΔE_{EC} for eq 8 for R = methyl predicts $\Delta H_f°$ for protonated 2-fluoropropane to be >100 kJ mol^{-1} above that of free isopropyl cation plus hydrogen fluoride.)

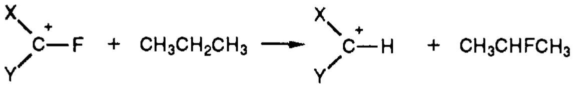
Stabilities of Cations. Fluorine substitution of a carbon–carbon multiple bond increases its proton affinity. Fluoroethylene has a proton affinity 15 kJ mol^{-1} greater than that of ethylene.[6] 2-Fluoropropene has a proton affinity 12 ± 6 kJ mol^{-1} greater than that of propene[21,27] (24 kJ mol^{-1} from SCF calculations at 6-31G**). Fluoroacetylene has a proton affinity 45 kJ mol^{-1} greater than that of acetylene[8,32] (19 kJ mol^{-1} from SCF calculations at 6-31G**). Substituent effects have been dissected into three parameters by Taft and his co-workers:[33] one (σ_F) dependent upon the electric field (and its sign), one (σ_α) dependent upon the magnitude of the electric field (but not its sign), and one dependent upon resonance effects (σ_R). The field effect of fluorine (relative to that of hydrogen) can be described as being destabilizing toward positive charge. Moreover fluorine is the only substituent whose contribution from electrical polarizability (σ_α) is less stabilizing than that of hydrogen. The increase in proton affinity of multiple bonds from monofluorination must therefore be due to resonance effects.

Table VIII. Best Estimates for Heats of Formation for Fluorine-Containing Ions[a]

ion	$\Delta H_f°$	method
12	660	equiv cores
13	650	ab initio
14	670	ab initio
15	640	ab initio
18 (n = 1)	660	equiv cores
18 (n = 2)	555	equiv cores
18 (n = 3)	515	equiv cores

[a] Rounded off to the nearest 5 kJ mol^{-1}.

As a substituent on an sp^2 cation center, fluorine is portrayed by our NBO calculations[18] as donating electron density from its lone pairs and withdrawing inductively via its σ-bond. The net result can be described as a superposition of these two effects. When another n-donor heteroatom (nitrogen, as in ion **10**, or chlorine, as in ion **12**) is also attached to the cationic center, classical resonance structures place most of the positive charge on that heteroatom, which is β to the fluorine, where the σ-electron withdrawing effect greatly outweighs lone pair donation.



(13)

This picture can be tested by considering the calculated activation barrier for rotation about the C=N bond of ion **10** relative to $\Delta H^\ddagger$ for $CH_2NH_2^+$ (equation 10). First consider the metathesis depicted in eq 13. For a planar ion where X = hydrogen and Y = NH_2, eq 13 is exothermic by 30–35 kJ mol^{-1} from equivalent cores (22 kJ mol^{-1} from 6-31G** SCF energies). Once the NH_2 has been rotated 90°, there is no longer any double-bond character in the C–N bond. We would expect that eq 13 for such a nonplanar transition state should have about the same ΔH as when X and Y are hydrogen or alkyl, for which it is endothermic by 30–35 kJ mol^{-1}. We predict that the combined substituent effects on planar $CHRNH_2^+$ and on its 90° rotamer should lead to a $\Delta H^\ddagger$ value for R = F that is 55–70 kJ mol^{-1} lower than $\Delta H^\ddagger$ for R = H. The SCF calculation at 6-31G** gives a value of $\Delta H^\ddagger$ (**10**) that is 71 kJ/mol lower than $\Delta H^\ddagger$ ($CH_2NH_2^+$). This is to be compared with the lowering of the barrier (by 95 kJ/mol) calculated to result from conjugation with a C=C double bond in the case R = vinyl.

Now we turn to fluoronium ions, where positive charge is localized on fluorine. In eq 6 a symmetrical ion ($R_1 = R_2$) gives good agreement between SCF and equivalent-cores estimates. Unsymmetrical dialkylfluoronium ions exhibit substantial effects as consequences of geometrical relaxation, and we feel that SCF estimates are to be preferred to the method of equivalent cores in these cases. The values of ΔE_1 for ions **4** and **13** are slightly higher than the equivalent-cores estimates, but, as the first two entries in Table VI show, the SCF values of ΔH are much lower than predicted by equivalent cores.

On the basis of calculated ΔH for isomerization at 6-31G**, the order of stability of the three most stable acyclic $C_3H_6F^+$ isomers is **1** > **2** > **14**, with estimated $\Delta H_f°$ values summarized in Table VIII. Since isomerization of **1** to fluoretanium is not an isodesmic reaction we estimate the heat of formation of fluoretanium (**18**, n = 1) using eq 6. SCF and empirical estimates agree within 10 kJ mol^{-1}. Estimated on the basis, $\Delta H_f°$ for fluoretanium is slightly lower than for ion **14**, even though its SCF electronic energy is 48 kJ mol^{-1} higher.

We conclude that ion **2**, ion **14**, and fluoretanium all have heats of formation within 10 kJ mol^{-1} of one another. The ion–molecule complex of hydrogen fluoride with allyl cation, **15**, is calculated to be more stable than any of these, $\Delta H_f°$ = 640 kJ mol^{-1} based on its electronic energy (which is 38 kJ mol^{-1} below that of free allyl cation and hydrogen fluoride). Apart from ion **1**, no stable $C_3H_6F^+$ isomer has ever been reported,[2] which raises the question as to whether, in addition to being thermodynamically unstable,

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(31) Siggel, M. R. F.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *46*, 249–264.

(32) Kloster-Jensen, E.; Pascual, C.; Vogt, J. *Helv. Chim. Acta* **1970**, *53*, 2109–2118.

(33) Taft, R. W.; Abboud, J. L. M.; Anvia, F.; Berthelot, M.; Fujio, M.; Gal, J.-F.; Headley, A. D.; Henderson, W. G.; Koppel, I.; Qian, J. H.; Mishima, M.; Taagepera, M.; Ueji, S. *J. Am. Chem. Soc.* **1988**, *110*, 1797–1800.

the other isomers may be kinetically labile as well.

For symmetric, cyclic ethers the method of equivalent cores agrees well with ab initio calculations for three- and four-member rings. Since the O_{1s} ionization energies of tetrahydrofuran and tetrahydropyran are the same (within experimental uncertainty) as that of oxetane, we feel justified in inferring that the strain energies for four-, five-, and six-member cyclic fluoronium ions are the same as for the isoelectronic ethers.

(14)

18 19

Will cyclic fluoronium ions be stable with respect to the ring opening shown in eq 14? For large n, where the effects of ring strain and fluorine substitution of the ring-opened cation can be neglected, eq 14 should be endothermic by approximately 65 kJ mol^{-1}. Estimated heats of formation for fluorolanium (**18**, $n = 2$) and fluoranium (**18**, $n = 3$) are given in Table VIII. If there is no effect from fluorine substitution of the linear isomers **19**, then eq 14 is endothermic by 35 kJ mol^{-1} for $n = 2$ and by 55 kJ mol^{-1} for $n = 3$.

The combined heats of formation of 1-methylallyl cation and hydrogen fluoride are 560 kJ mol^{-1}.[27] Therefore ions **13** and **19** ($n = 2$) are thermodynamically unstable with respect to elimination. But unless there is a lower energy decomposition pathway than via eq 14, fluorolanium (**18**, $n = 2$) should be kinetically stable, with a barrier that is at least as high as the endothermicity of eq 14.

What experimental evidence supports the existence of kinetic barriers? Elimination of hydrogen fluoride is often a facile process, and it seems reasonable to ask whether thermodynamically unstable fluorine-containing cations can nevertheless be kinetically stable. The answer is affirmative. We estimate the heat of formation of the higher homologue of ion **1**, $(CH_3CH_2)_2CF^+$, to be $\Delta H_f° > 510$ kJ mol^{-1} (by analogy to the relative heats of formation of *sec*-butyl and isopropyl cations[27]), while the heat of formation of 1,3-dimethylallyl cation plus that of hydrogen fluoride is 500 kJ mol^{-1}.[27] The $(CH_3CH_2)_2CF^+$ ion is therefore thermodynamically unstable with regard to elimination, but (as we have elsewhere shown[34]) it is stable in the gas phase. We conclude from this example that thermodynamic instability does not necessarily dictate kinetic lability.

Conclusion

Empirical and ab initio estimates for $\Delta H_f°$ of a variety of monofluorinated cations are, for the most part, in agreement. With the exception of **1** all of the $C_3H_6F^+$ structures are estimated to be thermodynamically unstable with respect to **15**, the ion-molecule complex of allyl cation with hydrogen fluoride. Nevertheless, the possibility that kinetic barriers may exist provides a warrant for continued experimental efforts to observe isomers of **1**.

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Supplementary Material Available: Listing of Cartesian coordinates of optimized geometries (49 pages). Ordering information is given on any current masthead page.

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Chemical Bonding in Hypervalent Molecules. The Dominance of Ionic Bonding and Negative Hyperconjugation over d-Orbital Participation

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Abstract: Does sulfur form six covalent bonds in CH_3SO_2Cl, $F_3S{\equiv}N$ or carbon or phosphorus five bonds in $F_3C{=}O^-$, $F_3P{=}O$? After a brief history of the viewpoints on hypervalent bonding and a comparison of analysis methods (with CH_3SO_2Cl as example), natural population and natural bond orbital analysis is applied to a series of 32-valence-electron species of X_3AY type (CF_4, F_3NO, O_3ClF, O_3PS^{3-}, F_3SN, etc.). The σ-bonding in these systems is found to be significantly ionic, and the strongly polar σ^*_{AX} orbitals are found to be more effective electron acceptors than the extra-valence $d_\pi(A)$ orbitals. Negative $\pi_Y \rightarrow \sigma^*_{AX}$ type hyperconjugation, which results in π_{AY} bonding, is thus the primary contributor to π_{AY} bonding in X_3AY species, with $\pi_Y \rightarrow d_\pi(A)$ overlap secondary. However, the d orbitals serve to polarize the σ^*_{AX} orbitals. This enhances π_{AY} bonding and diminishes σ^*_{AX} antibonding interactions and must be included to obtain a qualitatively correct description. The strength of π_{AY} bonding increases along the series F_3SiF, F_3PO, F_3SN, F_3ClC, but the latter species, as well as F_3IC and F_3TeC^-, are found computationally to be incapable of existence. By generalizing our discussion to n-coordinate $8n$-valence-electron species (HF_2^-, BF_3, ClO_4^-, F_4SO, F_5TeO^-, IF_6^+, $OXeF_6$, etc.) and their "reduced" analogues that have one or more lone pairs on the central atom (SF_4, IF_6^-, ClF_3, etc.), we provide a classification of hypervalent (and many nonhypervalent) molecules. The simple, qualitative bonding concepts for hypervalent molecules developed here supercede the inaccurate and misleading dsp^3 and d^2sp^3 models that are still in widespread use.

I. Introduction

What is the role of d functions in the bonding of "hypervalent" compounds of Si, P, S, and Cl?[1-20] Although the theoretical evidence against the traditional dsp^3, d^2sp^3 bonding models has become substantial,[10-15] recent work by Mayer and others[19,20]

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