Theoretical and Experimental Studies on the Tetrafluoroethylene Dication

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$C_2F_4^{2+}$ is accessible by charge stripping from $C_2F_4^{\cdot+}$ with $Q_{min.}$ = 19.0 eV for $C_2F_4^{\cdot+} \rightarrow C_2F_4^{2+}$ which is in good agreement with the vertical ionization energy of 19.33 eV predicted by *ab initio* molecular orbital calculations (4-31G//4-31G); according to these calculations the planar (D_{2h}) form of $C_2F_4^{2+}$ corresponds to the global minimum, being 3.5 kcal mol^{-1} (14.6 kJ mol^{-1}) more stable than its perpendicular (D_{2d}) isomer in distinct contrast to the analogous ethylene dication species for which the perpendicular form represents the global minimum on the $C_2H_4^{2+}$ potential energy surface.

Carbodications are an emerging class of remarkable molecules.[1] Many examples are known in solution,[2] and in the gas phase charge-stripping (C.S.) mass spectrometry[3] and other methods have led recently to the observation of numerous stable dications, including even small molecules whose coulombic repulsion is expected to be quite substantial.[4] High level *ab initio* molecular orbital (M.O.) calculations in conjunction with experimental studies have provided a detailed description of many features of these unusual species.

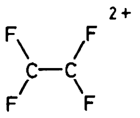
The ethylene dication $C_2H_4^{2+}$ provides a case in point; this has been thoroughly studied both experimentally[5] and theoretically.[1a] The perpendicular (D_{2d}) form dication is the global and the only singlet $C_2H_4^{2+}$ minimum, being 28.1 kcal mol^{-1} (MP3/6-31G**//6-31G* including corrections for zero-point energies; 28.0 kcal mol^{-1} at the 3-21//3-21G level)† more stable than the planar (D_{2h}) structure which corresponds to a rotational transition state. The source of stability of the perpendicular relative to the planar form of $C_2H_4^{2+}$ has been ascribed to hyperconjugation. In the D_{2d} isomer the two formally vacant orbitals at the carbon atoms are orthogonal and each interact hyperconjugatively with the corresponding vicinal CH_2 groups. This leads to the best charge distribution; positive charge is deflected to the periphery of the molecule and resides primarily on the more electropositive hydrogen atoms. The planar $C_2H_4^{2+}$ form lacks this stabilization; consequently it is much higher in energy, and also has distinctly different geometry. For example, the C–C bond of the planar form is 0.1551 Å longer than for the perpendicular one (6-31G*).

What happens when the hydrogen atoms are replaced by fluorine which is known not to stabilize cationic centres hyperconjugatively?[6] Can one generate $C_2F_4^{2+}$ species and, if so, what is the most stable structure? To answer these questions we have performed *ab initio* M.O. calculations using the split-valence 4-31G basis,[7]‡ as well as charge stripping experiments. The most relevant data are in Table 1.

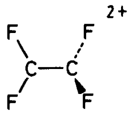
Table 1. Total energies (Hartree), geometries (bond lengths in Å, bond angles in degrees), and charge distributions of $C_2F_4^{2+}$, $C_2F_4^{\cdot+}$, and C_2F_4, derived from 4-31G//4-31G M.O. calculations.

Species	Energy	Geometry	Charge distribution
$C_2F_4^{2+}$ (**1**), D_{2h}	−471.7452[a]	C–F 1.238 C–C 1.581 ∠FCC 118.4	F −0.09 C 1.18
$C_2F_4^{2+}$ (**2**), D_{2d}	−471.7396	C–F 1.240 C–C 1.575 ∠FCC 118.6	F −0.08 C 1.16
$C_2F_4^{\cdot+}$ (**3**), D_{2h}	−472.4245	C–F 1.284 C–C 1.394 ∠FCC 121.0	F −0.24 C 0.99
C_2F_4 (**4**), D_{2h}	−472.8035	C–F 1.334 C–C 1.296 ∠FCC 123.4	F −0.38 C 0.77

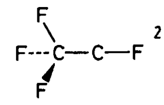
[a] The total energy of $C_2F_4^{2+}$, (D_{2h}) having the geometry of (**3**) has been calculated to be −471.7142 Hartree.



(**1**), D_{2h}



(**2**), D_{2d}



(**5**), C_{3v}

Replacement of hydrogen in ethylene by fluorine results in dramatic changes. (i) The global and the only minimum on the $C_2F_4^{2+}$ potential surface corresponds to the planar D_{2h} form (**1**), which is 3.5 kcal mol^{-1} more stable than the perpendicular D_{2d} structure (**2**); the latter has one and only one negative eigenvalue in the force-constant matrix, thus showing that (**2**) is the transition state for the rotation around the C–C bond. This finding is in distinct contrast with the results obtained for $C_2H_4^{2+}$ and is caused by the inability of fluorine to interact hyperconjugatively with the charge centres.

(ii) In line with the small energy difference between (**1**) and (**2**) the geometric features of (**1**) and (**2**) are also comparable. In either form the charges are mainly located on the carbon atoms which leads to long C–C bonds (1.581 and 1.575 Å).

(iii) The C–C bond of $C_2F_4^{2+}$ is substantially longer than that of $C_2F_4^{\cdot+}$ (**3**) and C_2F_4 (**4**) (1.39 and 1.30 Å), owing mainly to electrostatic repulsion. Conversely the decrease of the C–F bond lengths when comparing (**4**) with (**3**), (**2**), and (**1**) points to a mesomeric contribution of the lone-pair electrons of fluorine which interact with the formally empty orbitals at carbon in (**1**), (**2**), and (**3**).

(iv) The tetrafluoroethylidene dication $F_3C–CF^{2+}$ (**5**) (C_{3v} symmetry) is not found to exist on the 4-31G potential energy surface; during optimization it dissociates spontaneously to CF_3^+ (D_{3h}) and CF^+ ($C_{\infty v}$) ($E_{tot.}$ −335.3155 and −136.6307 Hartree†). For the analogous C_{3v} isomer of $C_2H_4^{2+}$ it was found[1] that $H_3C–CH^{2+}$ is likely also not be a stable species but to act as an intermediate in the hydrogen scrambling.

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† 1 cal = 4.184 J; 1 Hartree = 2.6255 × 10^6 J mol^{-1}; 1 eV = 9.6485 × 10^4 J mol^{-1}.

‡ The size of the $C_2F_4^{2+}$ system did not permit us to employ larger basis sets with polarisation functions and to include the effects of electron correlation. However, many structural and energetic data obtained for $C_2H_4^{2+}$ using 3-21G//3-21G and MP3/6-31G**//6-31G* basis sets are comparable[1a] except for systems having bridged structures, and reaction pathways which are associated with multiplicity differences.

(v) The vertical and adiabatic ionization energies for removing an electron from $C_2F_4^{\cdot +}$ (**3**) were calculated as I.E.$_{\text{v}}$ = 19.33 and I.E.$_{\text{ad.}}$ = 18.49 eV, respectively.† This is in excellent agreement with the experimentally derived $Q_{\text{min.}}$ value of 19.0 ± 0.1 eV.§

(vi) In spite of the high coulombic repulsion, dissociation of $C_2F_4^{2+}$ *via* charge separation to $C_2F_3^{+}$ and F^{+} has an endothermicity of *ca.* 118 kcal mol^{-1} [4-31G//4-31G energies for $C_2F_3^{+}$ (C_{2v}) and $^1F^{+}$ are −373.0231 and −98.5344 Hartree];¶ similarly, dissociation of $C_2F_4^{2+}$ to $C_2F_3^{2+}$ and $F^{\cdot}$ is energetically unfavourable by 87 kcal mol^{-1} [$C_2F_3^{2+}$ (C_{2v}), −372.3419; $F^{\cdot}$, −99.2655 Hartree]. The 4-31G//4-31G result for the thermochemistry of the process $C_2F_4^{2+} \rightarrow 2CF_2^{\cdot +}$[$\Delta H^{\circ}_{R}$, −81.6 kcal mol^{-1}; $CF_2^{\cdot +}$ (C_{2v}), −235.9377 Hartree] should be considered with great caution since the result is sensitive to correlation effects because of the multiplicity change.

Nevertheless, the theoretical estimation is in good agreement with experimental results. Indeed, the mass-analysed ion kinetic energy (M.I.K.E.) spectrum, *m/z* 50 ($C_2F_4^{2+}$), reveals a dished peak centred at E_0 which corresponds to the spontaneous dissociation $C_2F_4^{2+} \rightarrow 2CF_2^{\cdot +}$. The measured kinetic energy release, *T*, associated with this reaction is 3.47 eV which leads to an activation energy of 80 kcal mol^{-1} for this process. No signal corresponding to dissociation of $C_2F_4^{2+}$ to CF_3^{+} and CF^{+} was observed thus confirming the predicted inability to generate $F_3C{-}CF^{2+}$ (**5**). By admitting O_2 as a collision gas a single additional decomposition channel was observed which corresponds to the reaction $C_2F_4^{2+} + O_2 \rightarrow [C_2F_4^{2+}\cdot^{\cdot}] \rightarrow CF_3^{+} + CF + O_2^{\cdot +}$.

We have also studied computationally some triplet states of $C_2F_4^{2+}$ and found that they are unlikely to be generated in the charge stripping from $C_2F_4^{\cdot +}$. The triplets of either (**1**) and (**2**) are calculated to be at least 60 kcal mol^{-1} less stable than their corresponding singlet species, and the triplet state of (**5**) is, like the singlet, found to dissociate spontaneously. Moreover, ^{3}(**1**) and ^{3}(**2**) possess, according to the calculations, one long C–F bond (*ca.* 2.0 Å) which indicates that these species are likely to reside on a shallow potential minimum.

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§ The $Q_{\text{min.}}$ value, *i.e.* the energy to remove one electron from $C_2F_4^{\cdot +}$, has been determined in a C.S. experiment by using a VG analytical ZAB-2F mass spectrometer; mass-separated $C_2F_4^{\cdot +}$ ions of 8 keV energy were collided with O_2 molecules at a pressure of *ca.* 10^{-4} Torr. The products of the collision-induced reactions were studied by scanning the electrostatic analyser. For an accurate measurement of the ionization energy of the ion, the energy scale was calibrated by admitting toluene as a reference compound for which $Q_{\text{min.}}$ is known to be 15.7 eV for the process $C_7H_8^{\cdot +} \rightarrow C_7H_8^{2+}$ (F. M. Dorman and J. D. Morrison, *J. Chem. Phys.*, 1961, **35**, 575). The $Q_{\text{min.}}$ value was obtained by extrapolating to the base line of the high-energy side of both the main beam ($C_2F_4^{\cdot +}$ ions) and the charge-stripping peak, as recommend in ref. 3d, to prevent other possible processes.

¶ The endothermicity would be reduced to 19.3 kcal mol^{-1} if $^3F^{+}$ were generated [$E(^3F^{+})$ = −98.6914 Hartree].

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