A NON-EMPIRICAL LCAO-SCF-MO INVESTIGATION OF CROSS SECTIONS THROUGH THE POTENTIAL ENERGY SURFACE FOR THE $[C_2H_4Cl]^+$ SYSTEMS; COMPARISON WITH THE $[C_2H_5^+]$ AND $[C_2H_4F]^+$ SYSTEMS

D. T. CLARK*† and D. M. J. LILLEY

Department of Chemistry, The University, Durham

Abstract—Non-empirical LCAO MO SCF calculations are reported on cross sections through the $C_2H_4Cl^+$ system and comparisons are drawn with the $C_2H_5^+$ and $C_2H_4F^+$ systems. Barriers to rotation in the classical 1- and 2-substituted ethyl cations have been computed and an investigation made of the bridged chloronium and fluoronium ions. The results suggest that the relative stabilities of bridged ions with respect to the corresponding classical 2-substituted ethyl cations increase in the order H < F < Cl. The results are discussed in terms of available experimental data and consideration given to correlation and solvation energy effects.

INTRODUCTION

The electronic structures and reactivities of simple carbonium ions play a central role in physical organic chemistry and yet it is only in the past few years that adequate theoretical treatments of such systems have started to appear.[1,2] In previous papers[1,3-5] we have presented the results of *ab initio* molecular orbital calculations for cross sections through the potential energy surface for the systems $[C_2H_4X]^+$ where X = H or F. Valuable information has thereby been obtained on barriers to rotation in classical ions and their ease of interconversion. Such studies can provide insights invaluable to the experimentalist, even with regard to solvent effects since in principle it is possible to say a great deal about isolated ions in the gas phase and hence ascertain what can or cannot be ascribed to solvent effects. In this paper we described results for the system $[C_2H_4Cl]^+$ which form a most interesting comparison with those previously reported.

Method

Standard LCAO SCF Molecular Orbital theory has been used and the calculations performed with the IBMOL V[6] computer program implemented on an IBM 360/195. (Double precision has been used throughout this work.) The basis set[7] of 72 primitive gaussian functions consisted of optimized ten *s* six *p* for chlorine, seven *s* three *p* for each carbon and three *s* atomic sets for the hydrogen atoms. The 72 gaussian functions were then reduced to 26 contracted functions corresponding to contracted sets of four *s* two *p* on chlorine, three *s* one *p* on each carbon and one *s* on each hydrogen. (Ex-

ponents and contraction coefficients are in Table 1.) Preliminary calculations carried out on 2-chloro-ethyl cations with an STO 3G basis set and including *d* orbitals on chlorine indicated that *d* orbital participation is negligible as far as the classical ions are concerned. 3*d* orbitals on chlorine have therefore been neglected. This may not be entirely justified for the bridged chloronium ion and we will return to this point in section 5.

The geometries used for the carbon, hydrogen frameworks are, except where indicated, derived from those optimized in previous work upon the $[C_2H_4X]^+$ (X = H, F) systems, taking a standard C—Cl distance for the classical ions of 1·77 Å. Co-ordinates for typical species are given in Table 2.

Conformational processes in chloroethane

In order to test the adequacy of the basis set used for chlorine for describing conformational processes, calculations have been carried out on chloroethane. The great advantage of non-empirical calculations on conformational processes is that it allows a detailed analysis of component attractive and repulsive contributions to barriers to rotation or inversion.[8] The calculated barrier to rotation in chloroethane is shown in Table 3, where comparison is also made with fluoroethane and ethane in similar basis sets, together with the experimental values. The barriers are in reasonable agreement with the experimentally determined results and indicate that the basis set for chlorine is adequate for discussion of conformational processes. In examining component attractive and repulsive energy components to the barriers there are several ways in which the energy terms (*viz.*, nuclear electron attraction V_{ne}, nuclear nuclear repulsion V_{nn}, electron electron repulsion V_{ee} and kinetic energy T) may be grouped together to give components of

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*cf. Reference 1 and references therein.

†To whom correspondence should be addressed.

Table 1. Exponents and contraction coefficients for hydrogen, carbon, fluorine and chlorine

	Exponents				Contraction Coefficients		
Hydrogen	0·450038	D	01	Hydrogen	0·7048	D	01
S	0·681277	D	00		0·40789	D	00
	0·151374	D	00		0·64767	D	00
Carbon	0·9947	D	03	Carbon	0·72	D	−02
	0·16	D	03		0·473	D	−01
	0·3991	D	02		0·1819	D	00
S	0·1182	D	02		0·4474	D	00
	0·3698	D	01		0·4438	D	00
	0·6026	D	00		0·434	D	00
	0·1817	D	00		0·6859	D	00
	0·4279	D	01		0·1093	D	00
P	0·8699	D	00		0·4597	D	00
	0·2036	D	00		0·6302	D	00
Fluorine	0·2723	D	04	Fluorine	0·59	D	−02
	0·4164	D	03		0·42	D	−01
	0·9773	D	02		0·1792	D	00
S	0·2787	D	02		0·4544	D	00
	0·8712	D	01		0·4436	D	00
	0·1396	D	01		0·5064	D	00
	0·4209	D	00		0·6190	D	00
	0·1053	D	02		0·127	D	00
P	0·2188	D	01		0·4784	D	00
	0·4785	D	00		0·6129	D	00
Chlorine	0·286563	D	05	Chlorine	0·1558	D	−02
	0·4299	D	04		0·11941	D	−01
	0·976335	D	03		0·59685	D	−01
	0·274415	D	03		0·208871	D	00
S	0·890063	D	02		0·444010	D	00
	0·312371	D	02		0·388159	D	00
	0·776951	D	01		0·350098	D	00
	0·307933	D	01		0·730327	D	00
	0·651038	D	00		0·390248	D	00
	0·240798	D	00		0·782082	D	00
	0·150436	D	03		0·278870	D	−01
	0·347101	D	02		0·173468	D	00
P	0·104071	D	02		0·469717	D	00
	0·337330	D	01		0·485035	D	00
	0·748495	D	00		0·485239	D	00
	0·207855	D	00		0·648858	D	00

opposite phase.[8] In this paper the barriers have been decomposed by examining the relative magnitudes of

$$V_{att} = V_{ne} + V_{nn} + T \qquad V_{rep} = V_{ee}$$

The component energy terms for chloroethane are given in Table 4 together with those for fluoroethane and ethane for comparison. The results of a recent investigation by Allen[12] for fluoroethane and ethane are also included. In all cases the most stable conformer is staggered and the barriers are dominated by the repulsive terms.

For ethane and fluoroethane the relative magnitudes of the component attractive and repulsive terms are in reasonable agreement for the two investigations. Fig 1 shows a plot of the absolute magnitudes of the attractive and repulsive components in going from ethane to fluoroethane to chloroethane. It is clear from the figure that although the barriers to rotation in this series are quite similar, the absolute magnitudes of V_{att} and V_{rep} increase progressively in going from ethane to fluoroethane to chloroethane and this may be compared with the situation in the fluoro and chloro substituted ethyl cations discussed in the next section.

Conformational processes in chloro ethyl cations

Non-empirical calculations can provide a firm basis for understanding available experimental data more fully as has been illustrated in the previous section. In the case of reactive intermediates how-

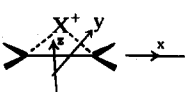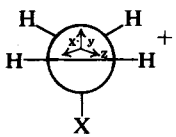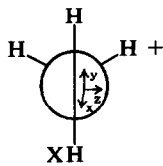Table 2. Co-ordinates (in a.u.) for typical species

	Atom	x	y	z
	X=Cl	0·0	0·0	3·77 (minimum Fig 7)
	X=F	0·0	0·0	2·83 (minimum Fig 7)
	C(1)	−1·392519	0·0	0·0
	C(2)	1·392519	0·0	0·0
	H(1)	−2·416765	−1·774045	0·0
	H(2)	−2·416765	1·774045	0·0
	H(3)	2·416765	1·774045	0·0
	H(4)	2·416765	−1·774045	0·0
	X=Cl	−1·110229	−3·135191	0·0
	X=F	−0·83898	−2·369205	0·0
	C(1)	0·0	0·0	0·0
	C(2)	2·963833	0·0	0·0
	H(1)	−0·689478	0·972474	−1·686771
	H(2)	−0·689478	0·972474	1·686771
	H(3)	3·988078	0·0	1·774046
	H(4)	3·988078	0·0	−1·774046
	X=Cl	4·626815	−2·880369	0·0
	X=F	4·211069	−2·160275	0·0
	C(1)	0·0	0·0	0·0
	C(2)	2·963833	0·0	0·0
	H(1)	−0·689478	0·972474	−1·686771
	H(2)	−0·689478	−1·947023	0·0
	H(3)	−0·689478	0·972474	1·686771
	H(4)	3·988078	1·774046	0·0

Table 3. Barriers to internal rotation (Kcal/mole)

	Calculated	Experimental
Ethane	2·72	2·93[9]
Fluoroethane	2·60	3·33[10]
Chloroethane	3·33	3·69[11]

ever, calculations can provide extremely valuable information on not only the nature of barriers to rotation but also the magnitudes of barriers which, for carbonium ions for example, are extremely difficult to measure experimentally.

For the 2-fluoroethyl cation for example our previous investigations[4] showed a substantial barrier (10·53 Kcals/mole) to rotation with the most stable conformer being eclipsed. This result has important ramifications for interpreting the chem-

istry of systems involving this carbonium ion. The results derived from non-empirical calculations contrast strongly with predictions based on simplistic physical organic arguments and illustrates the great value of rigorous theoretical treatments of such systems.

1-*Chloroethyl cation*. The results for the 1-chloroethyl cation are shown in Fig 2. There are two points of interest. Firstly the small barrier to rotation (0·53 Kcals/mole) which is comparable to that in the 1-fluoroethyl cation and secondly that the most stable conformer has chlorine eclipsing hydrogen and the least stable conformer is staggered, which is the parallel of the case for the 1-fluoroethyl cation.[4] Table 5 shows a comparison of the component energy terms for the fluoro and chloro species and also for the ethyl cation where the computed barrier is virtually zero. It is evident that for both the 1-chloro and -fluoro substituted

Table 4. Barriers to rotation and component energy terms for ethane, fluoroethane and chloroethane

		E_{TOT} (au)	$(V_{ne} + T)$ (au)	V_{ee} (au)	V_{nn} (au)	ΔV_{att}	ΔV_{rep}
Ethane	stag	−78·906247	−186·13054	65·377007	41·847286	0·0162	0·0205
	eclip	−78·901915	−186·15409	65·397540	41·854639	0·0111*	0·0152*
Fluoroethane	stag	−177·53239	−400·15366	143·00673	79·614547	0·0445	0·0486
	eclip	−177·52825	−400·23156	143·05534	79·647979	0·0411*	0·0452*
Chloroethane	stag	−537·475518	−944·019214	303·498782	103·04491	0·0723	0·0776
	eclip	−537·470215	−944·153704	303·576414	103·10707		

*Values taken from ref. 12 which used as a basis set, Gaussian lobe functions; for C and F (ten s, six p) contracted to (two s, two p); for H (four s) contracted to (one s).
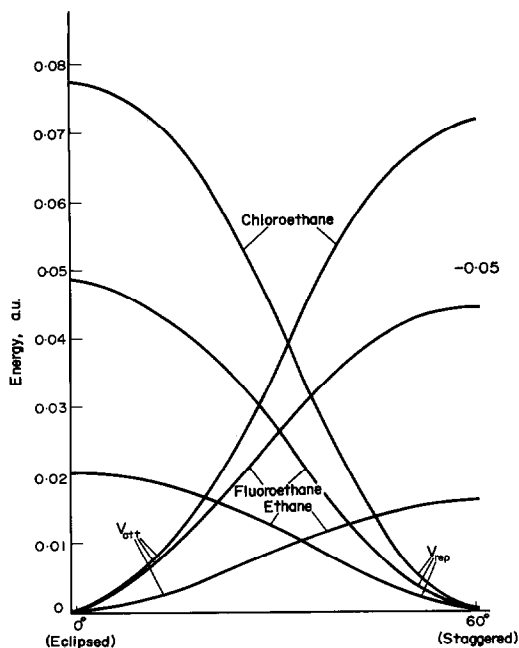
Fig 1. Variation with conformation of attractive and repulsive components of energy barriers of ethane, fluoroethane and chloroethane.

ethyl cations the rotational barriers are attractively dominated. We have noted previously that the behaviour of the 1-fluoroethyl cations closely resembles that of the isoelectronic acetaldehyde molecule,[13] where the most stable conformer has hydrogen eclipsing oxygen, and where the rotational barriers is also attractively dominated.

As in the case of the substituted ethanes the magnitudes of V_{att} and V_{rep} increases in going from the ethyl cation to the fluoroethyl cation to the

chloroethyl cation. Pople et al.[14] have also investigated the effect of methyl substitution on the barrier to rotation in the ethyl cation and the most stable conformer is again eclipsed (CCH eclipsing CH) although the barrier to rotation is now somewhat larger than for the parent (0·08 Kcals/mole). Although component energy terms have not been published it seems likely that this barrier is also attractively dominated.

2-Chloroethyl cation. The results for the 2-chloroethyl cation are shown diagrammatically in Fig 3. The rotational barriers of 0·91 Kcals/mole is seen to be slightly larger than in the 1-chloroethyl cation, and now the most stable conformer is staggered. These results contrast strikingly with those obtained for the 2-fluoroethyl cation, where the calculated barrier is much larger (10·53 Kcals/mole) and the most stable conformer has fluorine eclipsing hydrogen. A recent calculation on the 2-fluoroethyl cation by Radom[14] et al. (with an STO 3G basis set) has produced a rotational barrier of 9·31 Kcals/mole which is in good agreement with that produced by our calculations with slightly different geometry and basis set. Clearly the high barrier will have important ramifications for any reactions of this carbonium ion. These results suggest that the dominating influence upon the rotational barrier is different from that in 1-chloroethyl and the 1- and 2-fluoroethyl cations (the energy components are shown in Table 5).

By comparison with the 1-substituted cations, the absolute magnitudes of both V_{att} and V_{rep} are much larger for the 2-substituted ethyl cations, that for the chloro again being larger than for the fluoro species. The change in attractive components in going from the staggered (HH parallel to HH) to eclipsed (H eclipsing F or Cl) conformations is opposite in sign for the fluoro as compared to the chloro species being larger in absolute magnitude
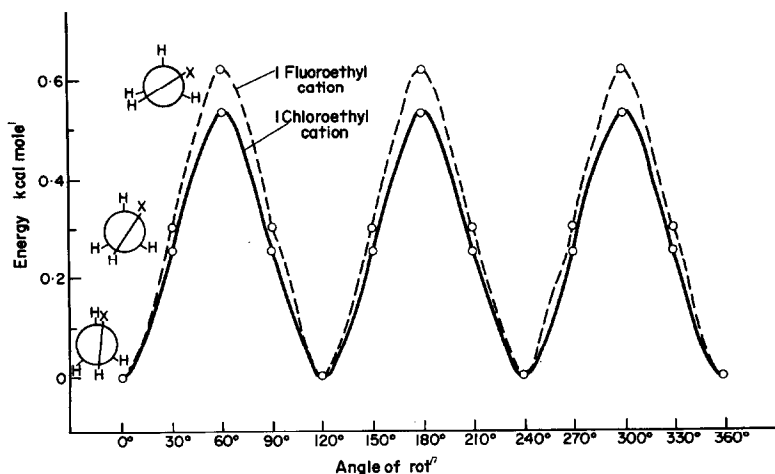

Fig 2.   Variation of total energy with conformation of 1-chloroethyl and 1-fluoroethyl cations.

Table 5. Barriers to rotation and component energy terms for 1- and 2-fluoro- and chloro-substituted ethyl cations

		E_{TOT} (au)	$(V_{ne} + T)$ (au)	V_{ee} (au)	V_{nn} (au)	ΔV_{att} (au)	ΔV_{rep} (au)
1-Fluoroethyl	0°	−176·58818	−373·98804	126·28470	71·11516	0·00669	0·00570
	60°	−176·58719	−373·96845	126·27900	71·10226		
1-Chloroethyl	0°	−536·519439	−911·061590	282·408806	92·133345	0·00918	0·00833
	60°	−536·518589	−911·023762	282·400473	92·104701		
Ethyl cation	stag	−77·911158	−170·37442	55·45621	37·00706	0·00002	0·00002
	eclip	−77·911153	−170·37441	55·45619	37·00706		
2-Fluoroethyl	0°	−176·52545	−377·73242	128·80992	72·39706	0·2470	0·2302
	90°	−176·50867	−377·40754	128·57972	72·31914		
2-Chloroethyl	90°	−536·473015	−916·756102	285·906789	94·376299	0·62752	0·628975
	0°	−536·471559	−917·552254	286·535764	94·544931		

for the latter. For the 2-chloroethyl cation however the change in repulsive terms is dominant so that overall the barrier to rotation is now much smaller than for the 2-fluoroethyl cation.

Rotational barriers in several 2-substituted ethyl cations have been investigated[15] with the computationally inexpensive STO 3G basis set. The results[15] in conjunction with those reported here show that with the exception of the 2-fluoroethyl cation the rotational barriers in simple 2-substituted ethyl cations tend to be fairly small, which accords with the classical view of organic chemists of free rotation in simple carbonium ions. To investigate the comparison between calculations employing different basis sets we have also investigated the 2-chloroethyl cation in an STO 3G basis set including $3d$ orbitals on chlorine (exponent 1·8). The results are in Table 6 and are in good agreement with those in Table 5. Part of the difference in calculated barrier to rotation may arise from the use of unoptimized exponents in the STO 3G basis set. (Exponents were evaluated by application of Burns rules[16]). The STO 3G basis set consisted of a least squares fit of Slater type orbitals to three gaussian functions. The Slater exponents being:

Cl	1s	16·5239	2s	5·7152	3s	2·3561
	2p	6·4966	3p	2·0387	3d	1·80
C	1s	5·6727	2s	1·6083	2p	1·5679
H	1s	1·2000				

For none of the occupied orbitals is there significant d orbital participation on chlorine and for the

*The results in Fig 11 of ref. 1 are in error, an eclipsed and staggered conformation having been inadvertently exchanged.

classical chloroethyl cations the role of $3d$ orbitals is that of providing polarization functions for the s, p basis set. The results for the STO 3G basis set are included for comparison in Fig 3.*

Relative energies of 1- *and* 2-*substituted ethyl cations.* For both chloro and fluoro substituted species the 1-substituted carbonium ion is more stable due to the stabilisation of the electron deficient centre by delocalisation from the lone pair orbital on halogen. The computed energy differences between the 1- and 2-substituted species are 39·36 Kcals/mole and 29·23 Kcals/mole for the fluoro and chloro species respectively. Some measure of the relative electronic effects of fluorine and chlorine in the 1- and 2-substituted ethyl cations may be obtained by comparing the relative energies for the processes RH → R⁺ + H⁻, taking the reaction for ethane as the energy reference. The results are shown in Table 7. The results seem chemically very reasonable, halogen attached to the electron deficient centre stabilising the 1-substituted cations relative to the 2-substituted species where the substituent exerts a destabilising influence. From mass spectrometric appearance potentials, Martin and Taft have estimated[17] that for the methyl cation replacement of H by F or Cl stabilizes the resulting ion by 27 ± 3 and 30 ± 4 Kcals mole⁻¹ respectively. These values are in reasonable agreement with those reported here.

The electronic structure of bridged onium species

Electrophilic addition of the hypothetical electrophiles F^+ or Cl^+, or suitable precursors, to ethylene could initially produce either the classical 2-fluoro or chloro ethyl cations, or a bridged fluoronium or chloronium ion. The experimental evidence[18] for the existence of the bridged chloronium

Table 6. 2-Chloroethyl cation – energy components from STO 3G calculations

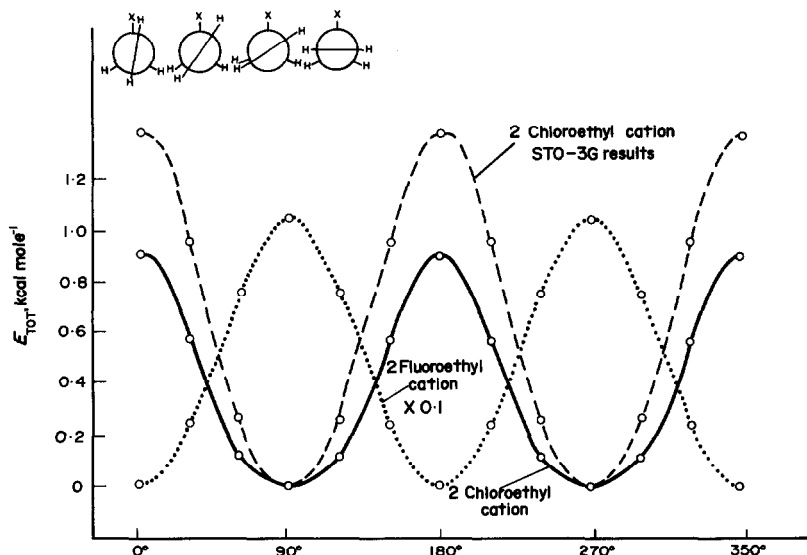| Rotamer	E_{TOT} (au)	$(V_{ne} + T)$ (au)	V_{ee} (au)	V_{nn} (au)	ΔV (au)	ΔV_{rep} (au)
H eclip Cl	−531·501796	−912·860089	286·813362	94·544391	0·6170	0·6192
HH parallel to HH	−531·504024	−912·074439	286·194116	94·376299		

Fig 3. Variation of total energy with conformation of 2-chloroethyl and 2-fluoroethyl cations, and variation of total energy (STO 3G) with conformation of 2-chloroethyl cation.

Table 7. Stabilizing and destabilizing influence of fluorine and chlorine substituents in ethyl cation

	ΔE_{rel} Kcals/mole
CH_3—CH_3 —→CH_3—CH_2^+ + H^-	(0·0)
CH_3—CH_2F ⟨→CH_3—CHF^+ + H^-	−29·5
→CH_2—CH_2F + H^-	+9·9
CH_3—CH_2Cl ⟨→CH_3—$CHCl^+$ + H^-	−22·0
→CH_2—CH_2Cl + H^-	+7·2

ion is fairly unequivocal, and there is a certain amount of evidence for the corresponding fluorine species also. The relevant portion of Olah's NMR studies[18] on the ionization of 2-halo-3-fluoro-2,3-dimethyl butanes in SO_2/SbF_5 is summarised in Fig 4. The production of bridged chloronium, and also bromonium and iodonium ions is strongly supported by the data. However in the case of the fluorine containing species Olah argued that the results are best explained in terms of a rapidly equilibrating pair of classical ions involving the intramolecular transfer of fluorine, rather than a bridged fluoronium ion. Even if this were the only interpretation of the NMR data however, it is difficult to avoid an intramolecular rearrangement that does not involve a species looking very much like a bridged fluoronium ion. Since the postulated intramolecular 1,2-fluorine shift has to occur rapidly at −90° to be compatible with the experimental observations, it is clear that even if Olah's interpretation is correct the energy difference between a classical 2-fluoroethyl cation and bridged fluoronium ion must be small. The NMR data on which this conclusion is based, however, are by no means incompatible with the postulate of a bridge fluoronium ion. A prime difficulty involved in inter-

preting the data in Fig 4 in terms of rapid intramolecular 1,2-fluorine shifts arises on consideration of other possible competitive rearrangements. For example 1,2-methyl shifts which are known to be extremely facile could lead to the ion $C(Me)_3$-C^+MeF. The NMR data clearly rules this out, however independent evidence would suggest that if classical ions are involved then this should be the thermodynamically most stable species. For example Fig 5 shows some experimental data concerning the ionisation of 1-fluoro-2-methyl-2-propanol in Magic acid,[2] together with a postulated mechanism to explain the formation of the product ion in which a fluorine atom and a methyl group stabilize the electron deficient centre. This is thermodynamically more stable than the initially formed ion with two methyl groups attached to the electron deficient centre with the fluorine atom attached to the other carbon exerting a destabilising influence.

Independent evidence for the existence of bridged halonium ions comes from studies of halogen as a neighbouring group in solvolysis reaction. For example, the large rate enhancement in the solvolysis of 2-halocyclohexyl brosylates[22] for the *trans* relative to the *cis* isomers coupled with the retention of configuration in the solvolysis products can be understood in terms of bridged bromonium and iodonium ions.

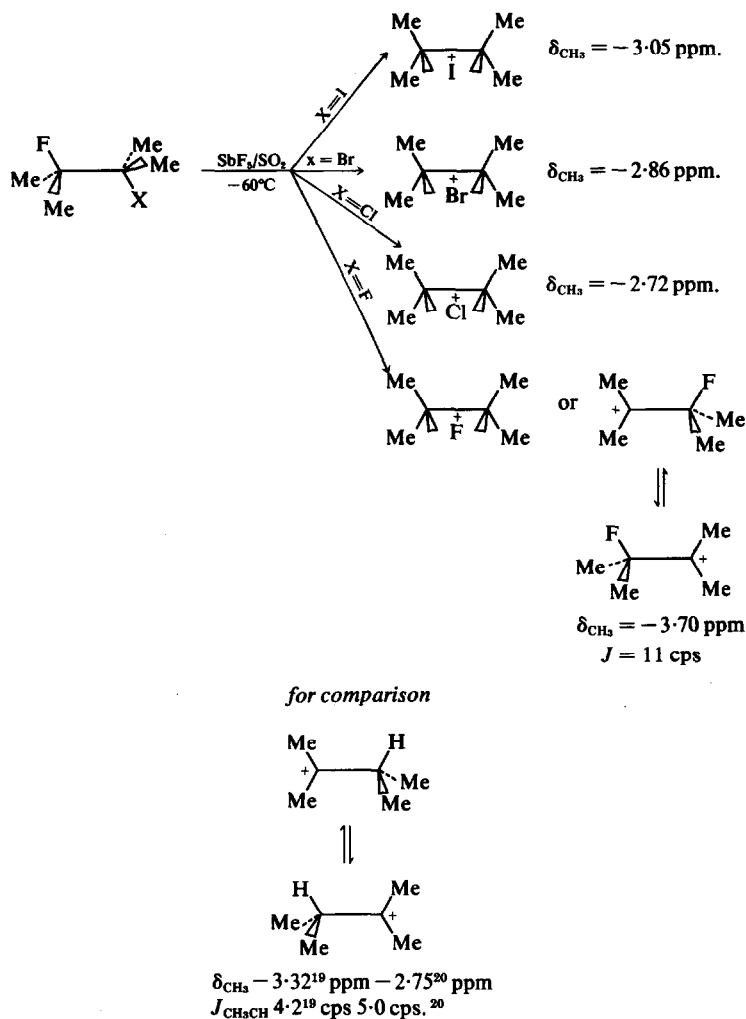Further evidence is forthcoming from the stereo-

Rate enhancement *trans/cis*   800   2,700,000
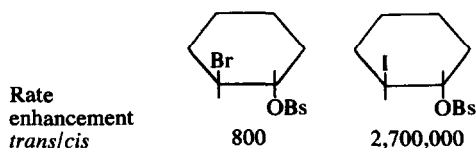
Fig 4. Summary of the NMR investigation by Olah *et al.*[19] of the ionisation products of 2-halo-3-fluoro-2,3-dimethyl butanes in SO_2/SbF_5.
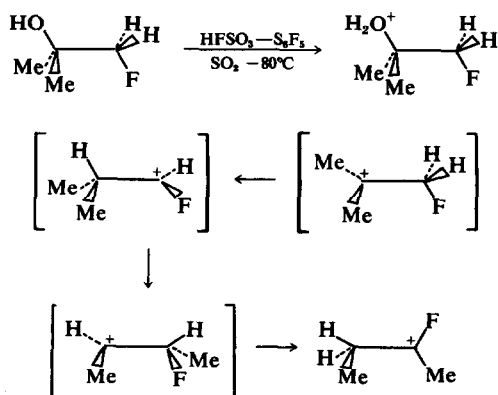

Fig 5. Suggested mechanism for the ionisation of 1-fluoro-2-methyl-2-propanol in Magic acid.[21]

chemistry of electrophilic additions to alkenes[23–26] (*cf.* Fig 6). In general it has been found that when the electrophile (designated X⁺) is formally Br⁺, I⁺ and RS⁺ addition occurs in a *trans* fashion, this usually being interpreted as being due to the formation of bridged ions. However when X⁺ may be formally regarded as H⁺, F⁺ and Cl⁺ the situation is less clear cut and examples are known of stereospecific *trans* and stereoselective *cis* additions. This is taken to indicate the intervention of bridged or classical ions depending upon the structure of the olefin. From the available data the inference may be drawn that the absolute stabilities of bridged ions relative to the corresponding classical ions almost certainly increases in the order H < F < Cl. Calculations on bridged halonium ions, therefore, are clearly of considerable interest.
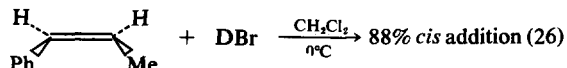
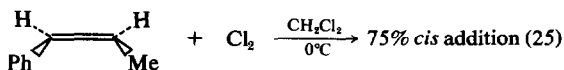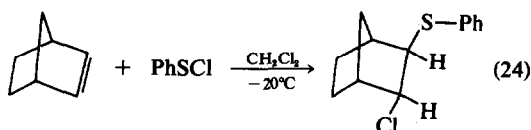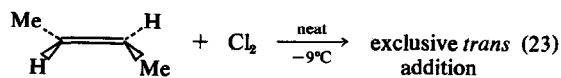Fig 6. Examples of stereospecific *trans* and stereoselective *cis* electrophilic addition to olefins.

Fig 7. Variation of total energies of fluoronium and chloronium ions as a function of the distance (in a.u.) of the bridging halogen atom from the centre of the CC bond.
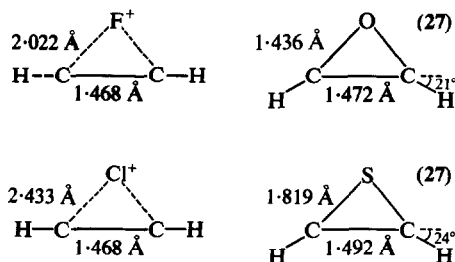

Fig 8. Partially optimised geometries of fluoronium and chloronium ions, with the experimental (microwave) geometries of oxirane and thiirane for comparison.

Computer limitations have not allowed us to optimize fully the fluoronium and chloronium ion geometries. As a reasonable starting point however we have used the previously optimized geometry of the ethylene fragment of bridge protonated ethylene and investigated the energies of bridged fluoronium and chloronium ions as a function of the distance of the halogen atom from the centre of the CC bond, Fig 7. The geometries obtained are shown in Fig 8, together with those of oxirane and thiirane for comparison, although the protonated forms of these which are isoelectronic with the fluoronium and chloronium ions respectively, would provide a more instructive comparison, were their geometries available. In both cases the computed carbon-halogen bond lengths are considerably longer (~ 0.6 Å) than the respective carbon-oxygen and carbon-sulphur bond lengths in oxirane and thiirane. The carbon-carbon bond lengths (1·468 Å) employed in these calculations is that previously optimized for bridge protonated ethylene and falls within the same range as those in the oxygen and sulphur heterocycles. For the latter the hydrogens are bent back by $\sim 21°$ and $24°$ respectively and the neglect of this factor in the partial geometry optimization for the bridged halonium ions, is likely to be the single most important deficiency. However on the basis of the much larger bond lengths between carbon and heteroatom for the bridged ions the out of plane bending of the hydrogens should be quite small and in the case of bridge protonated ethylene itself our own work[3] and that of others indicate that the ethylenic fragment is planar although small deformations from planarity are energetically inexpensive. Pople[28] and Pfeiffer[29] in their calculations (on bridge protonated ethylene) for example, have found small displacements 2·5°
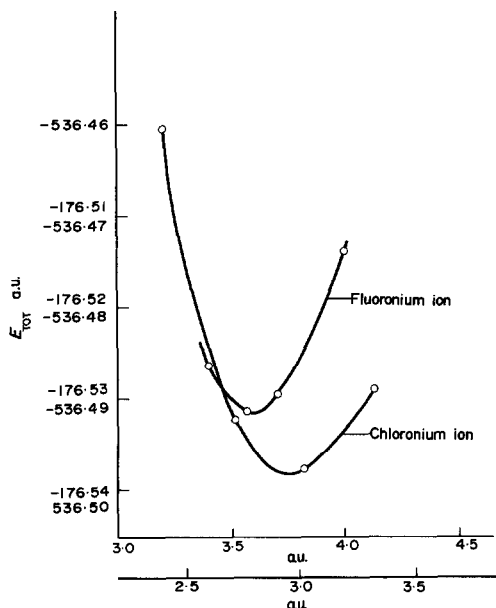
and 3° respectively) to be energetically favourable, however the energy lowering is very small (~ 0.3 Kcals/mole). It seems likely therefore that the out of plane bending in the bridged ions will be small and that our calculations provide a reasonable approximation to the geometry of these systems.

For bridged ions of the onium type the halogen is formally in a valence state higher than normal and thus d orbitals might be expected to become relatively more important compared with the classical ions. However, recent detailed calculations on S protonated thiirene[30] (which is isoelectronic with the analogous chlorine-bridge acetylene species), with an extended basis set show that d orbitals on second row atoms do not play a major role in understanding structure and bonding in such species. Both the neglect of $3d$ orbitals in the bridged species and the incomplete geometry optimizations will tend to underestimate the energies of the bridged

ions with respect to the classical substituted ethyl cations. Our calculations, therefore, should indicate a lower limit for the relative stability of the bridged with respect to the classical ions.

Fig 9 shows the relative energies of bridged and classical species for the $[C_2H_4X]^+$ (X = H, F, Cl) system obtained from our calculations. In the case of bridge protonated ethylene, both our own work[3] and that of others[25,26] have shown that the classical ethyl cation is the lower in energy. Indeed our results[3] suggest that bridge protonated ethylene is a good approximation to the transition state for the 1,2 proton shifts in ethyl cation. When X^+ is F^+ and Cl^+ it is clear from Fig 9 that in both cases the bridged halonium ion is predicted to be more stable than the 2-substituted ethyl cation. Furthermore, the relative stability of the halonium ion with respect to the 2-substituted classical ion is rather greater in the case of chloronium than for the fluoronium ion. (The inclusion of d orbitals would be expected to increase this effect.)

Extensive studies of barriers to rotation about

carbon–carbon single bonds in ethane and substituted ethanes have indicated that the absolute magnitude of such barriers and the contributing factors may be quantitatively described within the Hartree Fock formalism.* Indeed in general it has been found that in discussing processes in which the number of electron pairs do not change, correlation energy corrections are relatively small. We may anticipate that since the classical ions and corresponding bridged species discussed above possess the same number of electron pairs that correlation energy differences between species should also be relatively small. The calculated energy differences between the classical 2-substituted ethyl cations and the corresponding bridged ions are also relatively small (the energetic preference for the bridged ion in the case of the chlorine species is however quite substantial) and since there is a change in the degree of connectivity in proceeding from one to the other, small changes in correlation energy might become of some importance. A crude attempt has been made to investigate the possibility in the case of the bridge protonated ethylene and bridged-fluoronium ions and their respective classical ions. This represents

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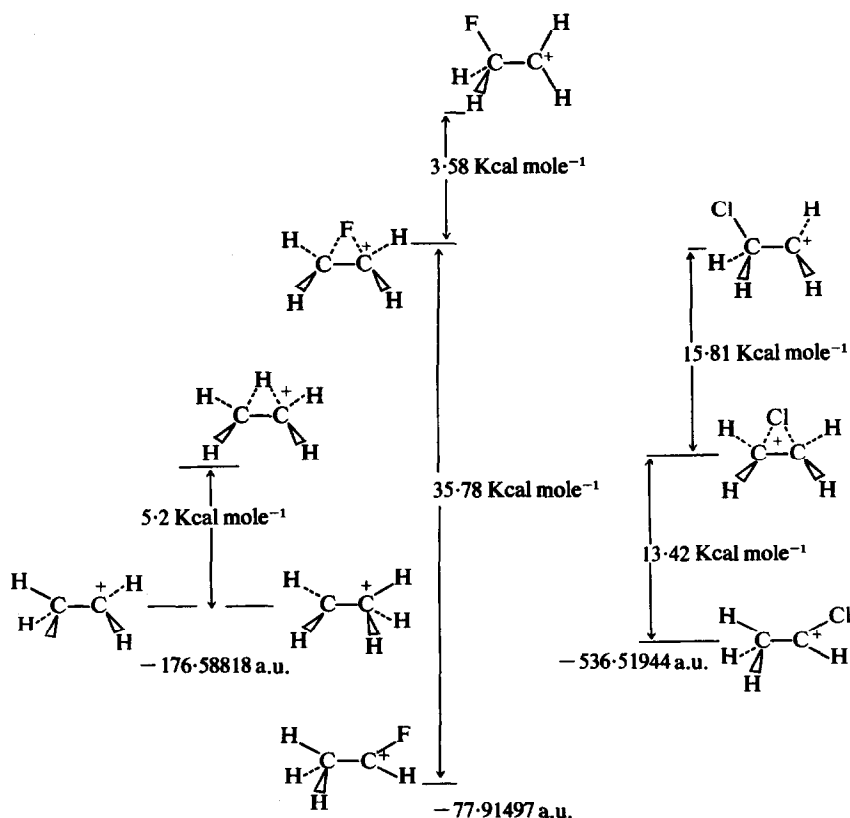*cf. Reference 2 and references therein.

Fig 9.   Relative total energy differences (drawn to scale) between bridged halonium ions and classical 1- and 2-substituted ethyl cations for $[C_2H_4X]^+$, X = H, F and Cl.

the extremes of two situations in which either the classical ion (in the case of hydrogen) or the bridged-ion (in the case of fluorine) are predicted to be the more stable from the SCF calculations.

Snyder and Basch[31] have shown how crude estimates of correlation energy differences may be obtained from pair correlation energies (established from atomic data) and appropriate population analyses, Eq. 1.

$$E_{corr} = \sum_i \epsilon_{ii} \tfrac{1}{2}\rho_i + \sum_{i<j} \epsilon_{ij}\rho_i\rho_j \qquad (1)$$

where ρ_i is the atomic orbital electron density for orbital i. The atomic orbital pair population of orbital i is then $\tfrac{1}{2}\rho_i$. The atomic orbital pair correlation energy ϵ_{ij} is the correlation energy of a pair of electrons in the same $(i = j)$ or different $(i \neq j)$ atomic orbitals. From atomic data Snyder and Basch have prepared a set of pair correlation energies for first row atoms (and hydrogen) the relevant data being given in Table 8.

From the form of Eq. 1 it is clear that E_{corr} may be split into two terms E_{corr}^{intra} and E_{corr}^{inter} depending on whether the pairs of orbitals are located on the same or different atoms. From atomic data only E_{corr}^{intra} may be estimated. However from extended basis set calculations and estimates of ΔE_{corr}^{intra} for a series of hydrogenation reaction Snyder and Basch showed that ΔE_{corr}^{inter} was in general of the same order of magnitude and opposite in sign and hence cannot be neglected. A roughly exponential dependence of ΔE_{corr}^{inter} on inter-atomic distance between the first row atoms was however evident from their data. In the case of the bridged ions and their classical counterparts studied here the best we can do is to make order of magnitude estimates of ΔE_{corr}^{intra}. The relevant data are collected in Table 9.

It is evident from this data that correlation energy corrections may well be of similar magnitude to the SCF calculated energy differences in the case of bridge-protonated ethylene and the fluoronium ion and their classical counterparts.

In the particular case of the bridged-chloronium ion it is of some interest to compare the results with recent work on the relative stability of the β thionyl cation and the corresponding bridged species (S

protonated thiirene). In this case the bridged ion is calculated to 10 Kcals/mole more stable than the corresponding classical β thiovinyl cation.[30] The bridge protonated species on the other hand is calculated to be ~ 20 Kcals *less* stable than the classical vinyl cation.[32] On this basis we might expect the chlorine species isoelectronic with S protonated thiirene to be comparable in energy with the substituted classical ion. This contrasts with the situation for the bridged-chloronium ion with respect to the 2-chloroethyl cation where the former is calculated to be considerably lower in energy. Overall the results seem reasonable since the theoretical calculations tend to show that the bridged species are relatively more stable with respect to the classical ions in going from acetylene to ethylene which is not entirely unexpected on the basis of consideration of ring strain.

Solvent effects. The calculations discussed in the previous section of course refer to isolated molecules in the gas phase and suggest (with the proviso that correlation energy terms cannot be adequately estimated) that the order of stability of bridged-ions with respect to classical ions is H < F < Cl, which is in keeping with the available experimental data. The latter however refer to solution phase measurements and it is therefore of some interest to consider in a rudimentary fashion the effect of solvent on these relative energies.

In a previous paper[1] we have shown how a simple model of solvent effects in which only the isotropic charge, dipole or dipole–dipole interactions are considered gives chemically sensible answers both for absolute and relative solvation energies of ions. The isotropic charge dipole, dipole-dipole solvent interaction may be estimated from Eq. 2

$$\Delta E_{solv} = -\Delta \sum \frac{q_i q_i}{2r_{ij}} (1 - 1/D) \qquad (2)$$

where the q_i's are the charges on each atom (from a Mulliken population analysis) and where r_{ij} is the interatomic distance between the atom i and the atom j except when i and j are identical. In this case r_{ij} represents the effective radius of the atom i. D is an effective dielectric constant of the solvent.

From the gross atomic charges and $\langle r \rangle$ values (from atomic Hartree Fock calculations) for the effective radii the calculated solvation energies for ethyl cation, bridge protonated ethylene, 1- and 2-fluoroethyl cations and bridged fluoronium ion are given in Table 10. (These are for a solvent of high dielectric constant i.e. $1 \gg 1/D$.)

The results seem chemically reasonable and suggest that the energy gap between the classical 1- and 2-fluoroethyl cations will be somewhat less in solution than in the gas phase. The results for the bridged-fluoronium ion would tend to suggest that in solution this species should be somewhat less favourable energetically than the classical 2-fluoro-

Table 8. Pair correlation energies in a.u.

| Pair | | Atom | | |
i	j	C	F	H
1s	1s	−0·0409	−0·0398	−0·0409
1s	2s	−0·0015	−0·0014	
1s	2p	−0·0015	−0·0016	
2s	2s	−0·0284	−0·0119	
2s	2p	−0·0139	−0·0084	
2p	2p	−0·0258	−0·0258	
2p	2p'	−0·0123	−0·0123	

Table 9. Estimates of ΔE_{corr}^{intra} for bridged and classical ions (in a.u.)

Atom		Bridge-protonated ethylene	Ethyl cation
C	1s–1s	−0·0818	−0·0818
	1s–2s	−0·0080	−0·0081
	1s–2p	−0·0183	−0·0181
	2s–2s	−0·0378	−0·0384
	2s–2p	−0·1128	−0·1132
	2p–2p	−0·0785	−0·0780
	2p–2p'	−0·0760	−0·0759
H	1s–1s	−0·0663	−0·0665
	Total	−0·4795*	−0·4800*

$\Delta E = -0.0005$ a.u. $= -0.31$ Kcals/mole (wrt classical ion)

*For comparison the total correlation energy for ethylene is estimated to be -0.5191 ± 0.0114 a.u. *cf.* L. C. Snyder, Robert A. Welch Foundation Bulletin, 29 (1971).

		Fluoronium ion	2-Fluoroethyl cation
F	1s–1s	−0·0398	−0·0398
	1s–2s	−0·0055	−0·0055
	1s–2p	−0·0164	−0·0165
	2s–2s	−0·0117	−0·0115
	2s–2p	−0·0851	−0·0839
	2p–2p	−0·0663	−0·0666
	2p–2p'	−0·1083	−0·1092
C	1s–1s	−0·0818	−0·0818
	1s–2s	−0·0079	−0·0078
	1s–2p	−0·0172	−0·0171
	2s–2s	−0·0375	−0·0368
	2s–2p	−0·1055	−0·1029
	2p–2p	−0·0740	−0·0735
	2p–2p'	−0·0688	−0·0688
H	1s–1s	−0·0512	−0·0533
	Total	−0·7770	−0·7750

$\Delta E = 0.002$ a.u. $= 1.26$ Kcals/mole (wrt classical ion).

ethyl cation. It should be emphasised however that the experimental observations relevant to this point concern[18] the tetramethyl substituted species in which the methyl substituents would be expected to exert two effects each favouring the bridged ion. Firstly the replacement of hydrogens by methyl groups should stabilize the bridged ion relatively more than the classical ion. This is evident from Olah's work[33] on trimethyl and 1,1-dimethyl halonium ions and their classical counterparts. Secondly, we may expect that in both the classical and bridged ions introduction of methyl groups will tend to lead to charge dispersal so that relatively the difference in solvation energies between classical and bridged ions will become smaller. On this basis and also on the basis of inconsistencies in interpreting the relevant NMR data in terms of

Table 10. Calculated (Eq. 2) solvation energies Kcals/mole

Ion	Solvation energy (Kcals/mole)
Ethyl cation	−95·0
Bridge-protonated ethylene	−92·6
1-Fluoroethyl cation	−112·4
2-Fluoroethyl cation	−126·6
Bridged-fluoronium ion	−105·8

rapidly equilibrating classical ions, we believe that the existence of the tetramethyl fluoronium ion is established in Olah's work.[18]

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