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IONIZATION POTENTIALS OF FLUORINE-SUBSTITUTED BENZENES, ETHYLENES, AND METHYL RADICALS

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Abstract—The "ω" technique, modified to take account of inductive effects, is used to calculate ionization potentials for fluorine- and other halogen-substituted benzenes, ethylenes and methyl radicals. The results indicate that the strong electronegative character of fluorine is indeed responsible for the unusual sequence of ionization potentials found for the poly-substituted fluorobenzenes. It is found that when the two highest occupied orbitals have nearly equal energies, removal of an electron from the highest orbital of the parent molecule does not necessarily lead to the most stable form of the ion. The calculations suggest that in the case of substituted ethylenes and methyl radicals it may be necessary to consider steric and field effects.

INTRODUCTION

A STUDY of the behaviour of compounds containing the element fluorine reveals many unusual features to the extent that the subject can almost be treated as a separate branch of chemistry. It has long been recognized that the peculiar behaviour of substances containing this element when compared with similar compounds involving the other halogens, is associated with the strong electronegative character of the fluorine atom. But, in spite of the many qualitative explanations based on this argument, few quantitative quantum-mechanical calculations have been published in the literature to substantiate this view. Apart from the inherent difficulties in treating large molecules satisfactorily by the methods of quantum mechanics, this has been partly due to the lack of experimental data for a wide range of related molecules. As far as data on ionization potentials is concerned, however, this is no longer the case, for recently Bralsford *et al.*[1] have published their results for the ionization potentials of a large number of fluorine-substituted ethylenes and benzenes as determined by photo-ionization. They were able to discuss their results satisfactorily in terms of the inductive and resonance effects associated with the presence of various fluorine substituents. Comparison with similar compounds involving other halogens indicated that the fluorine atom exerts a powerful inductive effect as would be expected from its high electronegativity.

The purpose of the present investigation is to see whether the qualitative description suggested by Bralsford *et al.* can be given a theoretical basis. If this can be accomplished then we should be in a better position to understand the properties and reactivites of carbon–fluorine bonds in general.

But there is also another problem closely related to this study; that is, the structure of the CF_3 radical.[2,3] This radical is involved in many reactions encountered in

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* Dedicated to the memory of Professor H. Stephen.

[1] R. Bralsford, P. V. Harris and W. C. Price, *Proc. Roy. Soc.* **258A**, 459 (1960).

[2] W. C. Price, T. R. Passmore and D. M. Roessler, *Disc. Faraday Soc.* **35**, 201 (1963).

[3] J. R. Majer, *Advances in Fluorine Chemistry* Vol. 2; p. 55. Butterworths, London (1961).

fluorine chemistry. While CF_3^+ is almost certainly planar, there has been some disagreement concerning the structure of CF_3. Thus even the dissociation of C_2F_6 into two CF_3 radicals—a relatively simple process—is not fully understood. In addition, the only ionization potential data on this and related radicals (CH_2F, CHF_2, CCl_3, etc.) are those obtained by electron impact.[3,4] It is generally appreciated that these are not as reliable as those obtained by spectroscopic or photo-ionization techniques. It is hoped that the results of the present investigation will give some measure of the reliability of these electron-impact values and perhaps throw light on the structure of these radicals.

METHOD OF CALCULATION

Recently, Streitwieser[5,6] has shown that the so-called "ω technique" is suitable for the calculation of ionization potentials of related hydrocarbons and other systems. This technique, which allows for the effects of the redistribution of electrons which must occur when ionization takes place, is a modification of the simple Hückel molecular-orbital method. As employed by Streitwieser, only the effects of the π electrons were considered. However, in fluorine-substituted systems where we expect large inductive effects through the σ bonds, some further modification is clearly necessary.

The essential feature of the ω technique as distinct from the simple M.O. theory is that the Coulomb integral, α_i, for the i'th atom is modified in the following way:

$$\alpha_i = \alpha_i^0 - \omega\beta\delta q_i^\pi \tag{1}$$

where

α_i^0 is the normal Coulomb integral,
β is the standard resonance integral,
δq_i^π is the excess (+) or deficiency (−) of π electrons on the i'th atom brought about by the presence of the other atoms in the molecule,

and ω is a fixed numerical parameter.

The usual way to use (1) is to begin with each α_i put equal to α_i^0 and to obtain the energies and charges in the molecular orbitals by solving the appropriate secular equations. These charges q_i lead, by (1), to a new set of α_i, and the process is now continued iteratively until the set of q_i's is self-consistent.*

Now it is clear that the Coulomb integrals α_i will depend not only on the π electron distribution, but also on the electron-donating or withdrawing power of a neighbouring atom transmitted through the σ bonds. Thus we have modified the expression (1) to include such effects:

$$\alpha_i = \alpha_i^0 - \omega\beta(\delta q_i^\pi + \delta q_i^\sigma) \tag{2}$$

where δq_i^σ is the excess or deficiency of electrons on atom i brought about by transmission of electrical effects through the sigma bonds. The δq_i^π will clearly be different

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* If convergence is slow—or even non-existent—it may be established by using one or other of the techniques described by C. A. Coulson and F. Wille, *Tetrahedron* in press (1966).

[4] F. P. Lossing, P. Kebarle and J. B. DeSousa, *Advances in Mass Spectrometry* p. 439. Pergamon Press, London (1959).

[5] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron* **5**, 149 (1959).

[6] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **82**, 4123 (1960).

in the molecule and the ion if a π electron is removed on ionization. But we have taken the δq_i^σ to be the same in the molecule and the ion—an approximation that should not be too serious if the π framework is large.

In order to complete the analysis for halogen-substituted molecules, the following parameters are required:

(i) values for $\alpha_C{}^0$ and $\alpha_X{}^0$, the standard Coulomb integrals,
(ii) values for $\beta^0_{C=X}$ and $\beta^0_{C=X}$, the standard resonance integrals,
(iii) values for δq^0_{C-H} and δq^σ_{C-X}, the sigma inductive charges associated with C—H and C—X bonds,
(iv) a value for ω.

As usual in this theory, all atomic overlap integrals are put equal to zero.

In the calculations reported in this paper, the $\delta q^\sigma_{C-X}(X \neq H)$ were derived from Pauling's electronegativity scale using the expression[7] $100\delta q = 16\,|x_A - x_B| + 3{\cdot}5\,|x_A - x_B|^2$. δq^σ_{C-H} was determined assuming a bond dipole moment of 0·4D in the $\overset{-}{C}$—$\overset{+}{H}$ bond: this value, $\delta q^\sigma_{C-H} = 0{\cdot}076$ is only slightly different from the value given by the above formula; i.e., $\delta q^\sigma_{C-H} = 0{\cdot}070$.*

$\alpha_C{}^0$, $\beta^0_{C=C}$, and ω were calculated from the ionization potential data on CH_3, C_2H_4, and C_6H_6 where we assumed (cf. Streitwieser[8]) that $\beta_{C-C}(C_2H_4) = 1{\cdot}1\beta^0_{C-C}(C_6H_6)$. This latter value is slightly less than that predicted from the formula of Coulson and Gołebiewski;[9] i.e., $\beta_{C=C}(C_2H_4) = 1{\cdot}17\beta^0_{C-C}$. Our method of derivation leads to a value for $\omega(\omega = 2{\cdot}03)$ considerably greater than that normally used by Streitwieser and others (i.e., $\omega = 1{\cdot}4$). Part of this difference can be attributed to the fact that we have used photo-ionization data rather than electron-impact data,[10] but the main factor seems to be the inclusion of a C—H inductive parameter. Thus if we compare the derived values for $\alpha_C{}^0$, $\beta^0_{C=C}$ and ω for both the Streitwieser and the Coulson-Gołebiewski β_{C-C} bond–distance relationships, we find that the inclusion of the δq^σ_{C-H} changes the value of ω substantially ($\delta\omega \simeq 0{\cdot}4$) but that of β^0_{C-C} hardly at all. On the other hand, for a given value of δq^σ_{C-H}, the β^0_{C-C} value is sensitive to the nature of the $\beta_{C=C}$ bond–distance relationship as would be expected.

It should be emphasised that as a result of our method of deriving these parameters we might expect our values to be applicable only to derivatives of these three molecules. This is because the ω technique considers only the effects of nearest neighbour interactions—the remaining interactions are apparently expected to be mysteriously incorporated into the ω parameter. But these interactions must be considerable, especially in ions, and would be expected to be quite different in, for example, the *cis* and *trans* modifications of the butadiene positive ion. In addition, some systems (e.g. styrene) will undergo on ionization substantial rearrangement of

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* The difficulties associated with the interpretation of C—H bond moments are well known (see, for example, C. A. Coulson, *Spectrochim. Acta* **14**, 161 (1959)). The direction and magnitude of the above value seemed to us to be reasonable for a C—H bond involving a trigonally hybridized carbon atom.

[7] C. A. Coulson, *Valence*, p. 141. Oxford University Press, 2nd. Ed. 1961.

[8] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, p. 135. New York, John Wiley and Sons, Inc., 1961.

[9] C. A. Coulson and A. Gołebiewski, *Proc. Phys. Soc.*, **78**, 1310 (1961).

[10] S. Ehrenson, *J. Chem. Phys.* **37**, 455 (1962).

the carbon atom framework, and it is probable that for such systems both bond orders and charge distribution would have to be made self-consistent. But calculations on naphthalene (calc: 8·25, expt: 8·12) and on anthracene (calc: 6·93, expt: 7·23) suggest that results using our parameters would compare favourably with those calculated by Streitwieser[5,6] or Ehrenson.[10]

The $\alpha_X{}^0$ were derived from ionization-potential data for the corresponding hydrogen halides (as suggested by Matsen[11] and adapted to the ω technique by Streitwieser[6]) but including the necessary sigma inductive effect.*

β^0_{C-F} was derived from the ionization potential of C_6F_6. If reliable bond distances were available, β_{C-F} for the fluoroethylenes could be estimated from $\beta^0_{C=F}$ using some relationship involving overlap integrals or an expression similar to that of Coulson and Gołebiewski for C—C bonds. However, this is not the case and so β_{C-F} for the fluoroethylenes was derived from the ionization potential of C_2F_4. The value (Table 1) is consistent with what we might expect from existing bond length measurements.[12,13]

In the case of the chloro- and bromoethylenes, two β_{C-X} integrals are required depending on whether one or two halogen atoms are bonded to the same carbon atom (*vide infra*). The necessary values were derived from ionization potential data[1] on 1,2-dichloroethylene, 1,2-dibromoethylene and tetrachloroethylene. The corresponding $\beta^0_{C=X}$ were obtained from the relationship $\beta_{C=F}/\beta^0_{C-F} = \beta_{C=X}/\beta^0_{C-X}$ where β_{C-X} refers to the —CX_2 system.

TABLE 1. VALUES OF PARAMETERS FOR M.O. CALCULATIONS

Coulomb integrals (eV)	Resonance integrals (eV)			Inductive parameters[a]
	Benzenes	Ethylenes	Radicals	
$\alpha_C{}^0 = -11·135$	$\beta_{C=C}$: −2·79	−3·069	—	$\delta q^{\sigma}_{C-H} = -0·076$
$\alpha_F{}^0 = -23·896$	$\beta_{C=F}$: −1·88	−2·11	−1·88	$\delta q^{\sigma}_{C-F} = -0·319$
$\alpha_{Cl}{}^0 = -19·381$	$\beta_{C=Cl}$ −0·95	−1·22[b]	−0·950[b]	$\delta q^{\sigma}_{O-Cl} = -0·089$
		−1·07[c]	−0·833[c]	
$\alpha_{Br}{}^0 = -18·017$	$\beta_{C=Br}$: −0·70	−0·90[b]	—	$\delta q^{\sigma}_{C-Br} = -0·051$
		−0·79[c]		
		$\omega = 2·03_1$		

[a] sign refers to carbon atom end of bond
[b] for —CHX system
[c] for —CX_2 system

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* The derivation is based on the assumption that a lone-pair p type electron is removed on ionization. This has not been definitely established for hydrogen fluoride. But if the first IP is, in fact, the removal of a bonding electron, that of the lone-pair electrons cannot be very much greater. Thus, the increase in our derived α's would be relatively small. It is unlikely, therefore, that our present results would be seriously affected particularly as the new α's would lead to correspondingly larger C=F resonance integrals as well. The effects of these two parameters on the calculated differences in IP for the two highest orbitals in substituted benzenes tend to neutralize one another (*vide infra*) so that the splittings in the fluoro-substituted benzenes should remain small.

[11] F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5243 (1950).

[12] *Tables of Interatomic Distances and Configuration in Molecules and Ions*, edited by L. E. Sutton. The Chemical Society, London (1958).

[13] D. Peters, *J. Chem. Phys.* **38**, 561 (1963).

In Table 1 we have collected together the parameters used in the present investigation.

RESULTS AND DISCUSSION

(a) *Substituted benzenes.* The calculated ionization potentials for the fluorobenzenes using the above parameters are reported in Table 2. These are given as the π energy of the ion minus the π energy of the molecule. When these are represented graphically as in Fig. 1, it is clear that the calculated values follow closely the experimental sequence. This suggests that it is indeed the large inductive parameter associated with the fluorine atom that is responsible for the unusual experimental sequence. In fact, without its inclusion in the calculation, it would not be possible to get $IP(C_6F_6) > IP(C_6H_6)$.

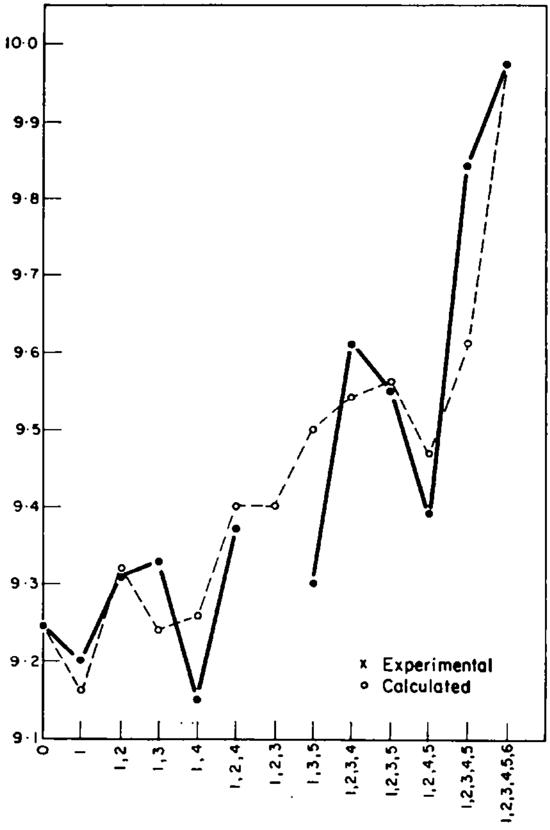

FIG. 1. Variation of ionization potential with position in substituted fluorobenzenes ———, experimental; - - - - calculated.

The above conclusion is supported by calculations on the chlorobenzenes and on bromobenzene (Table 2), where the inductive parameters required in the calculations are significantly smaller. While there is a scarcity of experimental data with which to make extensive comparisons, the fact that the calculations on the fluorochlorobenzenes and on *p*-fluorobromobenzene agree well with the experimental values, suggests that our parameters are at least internally consistent. It may turn out, however, that when more experimental results are available, these parameters will have to be slightly modified. Also included in Table 2 is the calculated ionization potential for the phenyl radical. Our results support the recent conclusion of Lossing *et al.*[14] that the ionization potential of this radical is less than that of benzene and gives us confidence that our C—H inductive parameter is of the correct sign and order of magnitude.

It should be pointed out that the measure of agreement with experiment reached in these calculations depends on the nature of the orbital from which the electron is removed. In most calculations of ionization potentials, the electron that is removed on ionization is considered to come from the highest occupied orbital of the parent molecule. However, in benzene the two highest occupied orbitals have exactly the same energies and in the substituted benzenes, they have very nearly the same energies. Thus it turns out that, within the framework of the ω technique, removing an electron from the top-occupied orbital in the parent molecule does not necessarily lead to the most stable form of the ion—providing yet another example of the well-known failure of Koopmans' theorem.[17] Indeed, the sequence of our calculated values would not follow so closely that exhibited by the experimental ones if we had not allowed for this possibility. For example, the removal of the electron from the highest occupied orbital in 1,4-difluorobenzene and 1,2,4,5-tetrafluorobenzene leads to their ionization potentials being greater than those of the corresponding isomers, yet the experimental values for these two molecules are actually considerably less. In

TABLE 2. IONIZATION POTENTIALS OF SUBSTITUTED BENZENES

	Expt.[a]	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.
	X = F		X = Cl		X = Br	
C_6H_6	9·245	(9·245)[b]	9·245	(9·245)[b]	9·245	(9·245)[b]
C_6H_5X	9·20	9·16	9·07	9·00	8·98	8·96
1,2-$C_6H_4X_2$	9·31	9·32	9·06	9·01		
1,3-$C_6H_4X_2$	9·33	9·24	9·12	8·99		
1,4-$C_6H_4X_2$	9·15	9·26	8·95	8·97		
1,2,3-$C_6H_3X_3$	—	9·40				
1,2,4-$C_6H_3X_3$	9·37	9·40				
1,3,5-$C_6H_3X_3$	(9·3)	9·50				
1,2,3,4-$C_6H_2X_4$	9·61	9·54				
1,2,3,5-$C_6H_2X_4$	9·55	9·56				
1,2,4,5-$C_6H_2X_4$	9·39	9·47				
C_6HX_5	9·84	9·62				
C_6X_6	9·97	(9·98)[b]				
1,2-C_6H_4FX	9·31	9·32	9·155	9·16		
1,3-C_6H_4FX	9·33	9·24	9·21	9·11		
1,4-C_6H_4FX	9·15	9·26	—	9·12	8·99	9·08
C_6H_5	$<$9·2[c]	9·09				

[a] all values from Ref. 1, 15 or 16.
[b] values used for parameters
[c] electron impact value[14]

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[14] I. P. Fisher, T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.* **86**, 2741 (1964).

[15] R. W. Kiser, *Tables of Ionization Potentials*, Report TID-6142. United States Atomic Energy Commission (1960).

[16] W. C. Price, private communication.

[17] J. R. Hoyland and L. Goodman, *J. Chem. Phys.* **33**, 946 (1960).

most other cases the energy difference between the two forms of the ion is not large so that reasonable agreement with experiment is obtained for either ionic species. Calculated ionization potentials referring to both ionic species are reported in Table 3. These are tabulated according to the symmetry type of the orbital involved in the ionization process (Fig. 2). The values marked with an asterisk refer to those cases in which the orbital concerned is the highest occupied orbital in the parent molecule.

A_2-type B_1-type

FIG. 2. Symmetries of highest occupied orbitals in substituted benzenes.

TABLE 3. DEPENDENCE OF IONIZATION POTENTIAL ON IONIC SPECIES

	A_2	B_1	Expt.
C_6H_5F	9·158*	9·163	9·20
1,2-$C_6H_4F_2$	9·33*	9·31	9·31
1,3-$C_6H_4F_2$	9·24	9·36*	9·33
1,4-$C_6H_4F_2$	9·35 (B_{3g})*	9·26 (B_{2g})	9·15
1,2,3-$C_6H_3F_3$	9·40	9·53*	—
1,2,3,4-$C_6H_2F_4$	9·54	9·64*	9·61
1,2,3,5-$C_6H_2F_4$	9·58*	9·56	9·55
1,2,4,5-$C_6H_2F_4$	9·47 (B_{3g})	9·64 (B_{2g})*	9·39
C_6HF_5	9·62	9·74*	9·84
C_6H_5Cl	9·04*	9·00	9·07
1,2-$C_6H_4Cl_2$	9·11*	9·01	9·06
1,3-$C_6H_4Cl_2$	8·99	9·12*	9·12
1,4-$C_6H_4Cl_2$	9·13 (B_{3g})*	8·97 (B_{2g})	8·95
1,4-C_6H_4FCl	9·24*	9·12	—
C_6H_5 Br	9·03*	8·97	8·98
1,4-C_6H_4FBr	9·22*	9·08	8·99

* highest occupied M.O. in parent molecule.

At first we found these results rather surprising. For example, in 1,4-difluorobenzene, one would have thought that removal of an electron from the B_{3g} orbital which involves only the four unsubstituted carbon atoms would lead to the lowest ionization potential. But it appears that the electron is removed from $\psi(B_{2g})$ in spite of the fact that this orbital involves not only the highly electronegative fluorine atoms but also the two carbon atoms to which the fluorines are attached. The latter are also strongly electronegative due to the inductive effect of the neighbouring fluorine atoms.

But we now believe that we understood the situation. In the B_{2g} orbital, there are two fluorine atoms attempting to delocalize their $2p_z$ electrons into the ring, a situation opposed by the repulsive forces between electrons. By removing an electron from this orbital, these repulsive forces are reduced, leading to a more stable form of the ion.

The calculations indicate that the differences in ionization potential for the two species may be quite small, although increasing for the heavier halogen substituents. It is possible, therefore, that photo-ionization techniques will not be able to detect such differences especially as there may be underlying vibrational structure and differences in ionization cross-sections. There is limited spectroscopic evidence, however, for such small differences. Hammond *et al.*[18] have observed two Rydberg series for fluorobenzene which lead to series limits differing by only 0·012 eV. This is the order of magnitude expected from our calculations (cf. 0·005 eV for fluorobenzene in Table 3).

It is possible that the 'ω' technique, as used in the present calculations, underestimates these differences. In particular, it does not take account of the fact that the C—X bond orders in the A_2 and B_1 ionic species are significantly different. Our method of deriving the C—X resonance integrals tends to minimize the effects of these differences, and it is conceivable that the incorporation of bond order self-consistency into the calculations could increase the splittings. In addition, it is unlikely that the 'ω' calculated from a carbon atom framework leads necessarily to an accurate modification of the Coulomb integral for a hetero atom. Since the charge distribution around the halogen substituent is substantially different for the two ionic species, the introduction of a new hetero 'ω' could affect the calculated splitting.

It might be worth pointing out that in benzene the two highest orbitals are degenerate so that the second IP probably corresponds to the removal of an electron from the A_{2u} orbital. We have calculated this to be 11·56 eV which agrees well with the experimental value of 11·49 eV.[19,20]

It is of interest to see how the relative stabilities of these ions depend on the values of the inductive, Coulomb and resonance parameters. Calculations* on mono-substituted and 1,4-disubstituted benzenes indicate that the relative stabilities of the alternative ionic species depend on these parameters in the following way:

(i) a large C=X resonance integral, β_{C-X},
(ii) a small Coulomb integral, α_X, and
(iii) a positive inductive parameter, $\delta q_{C=X}$,

favour the removal of the electron from a B_1 or B_{2g} type orbital, i.e. the orbital involving the substituent X. Now, the variation of the Coulomb integral and the inductive parameter should follow closely any trend in the electronegativity of X. We might, on the other hand, expect the resonance integral, β_{C-X}, to decrease as we go across or down the periodic table. Thus if we work our way along any row of the periodic table, the mesomeric effect and the inductive effect should reinforce one another; i.e. they will favour the stability of the ionic species formed when the electron is removed from an A_2 or B_{3g} orbital. But if we go up any column of the periodic table, the two effects should be opposed: the inductive effect favouring the

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* We are indebted to Mr. G. R. S. Harrison for these calculations.

[18] V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Disc. Faraday Soc.* **9**, 53 (1950).

[19] M. F. A. El-Sayed, M. Kasha and Y. Tanaka, *J. Chem. Phys.* **34**, 334 (1961).

[20] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.* 4434 (1964).

removal of an A_2 type electron but the mesomeric effect favouring the removal of a B_1 type electron. Our results (Table 3) for the halogen-substituted benzenes suggest that only in the case of fluorobenzene is it likely that the inductive effect will predominate—presumably due to the high electronegativity of the fluorine atom.

It is of interest to see how far these ideas regarding the effect of substituents on orbitals of different symmetry type can be used to interpret the effects of multiple substituents on ionization potentials. Consider the fluorotoluenes.[1,15] Fluorobenzene has an ionization potential of 9·20 eV and toluene one of 8·82 eV. It is not surprising then to find that the ionization potential of *o*-fluorotoluene has a value of 8.915 eV; that is, greater than toluene itself, for we have seen that additional fluorine substitution increases the ionization potential (Table 2). But the ionization potential of *p*-fluorotoluene (8·785) is less than that of toluene. This is not unexpected in view of our previous remarks, since if CH_3 hyperconjugation is involved, we would expect this to be the case. What is perhaps more interesting is the fact that the ortho and meta isomers have essentially the same ionization potential. This suggests that any hyperconjugation effect associated with the CH_3 group must in these cases be largely confined to an orbital resembling the A_2 orbital in the parent fluorobenzene, and therefore not directly involving the fluorine atom. For, if in both cases an A_2 type electron is removed on ionization, the ionization potential should not be significantly different. But, if in one case a B_1 type electron were removed and in the other an A_2 type, then it is unlikely that they would be the same.

TABLE 4. IONIZATION POTENTIALS FOR FLUORO-SUBSTITUTED ETHYLENES

	Calc.	Calc.†	Calc.‡	Expt.
CH_2CH_2	(10·51)*	(10·51)*	(10·51)*	10·51
CH_2CHF	10·53	10·39	10·35	10·37
CH_2CF_2	10·41	10·41	10·27	10·30
c-CHFCHF	10·47	10·22	10·25	10·25
t-CHFCHF	10·47	10·22	10·19	10·19
$CHFCF_2$	10·30	10·19	10·17	10·14
CF_2CF_2	(10·12)*	(10·12)*	(10·12)*	10·12

* expt. value used in deriving parameters

† includes an additional C—H parameter to reflect the effect of dipole induced by a F atom attached to same carbon centre.

‡ includes parameters for induced C—H dipoles in *cis* and *trans* positions.

(b) *Substituted ethylenes.* In Table 4, column 1, there are reported some calculated ionization potentials for fluoro-substituted ethylenes using the parameters listed in Table 1. The agreement with experiment is rather disappointing. However, there are a number of possible explanations for this. The value for the C=F resonance integral is that derived from the ionization potential of tetrafluoroethylene and inspection of the calculated values shows that the agreement for CF_2CH_2 and CF_2CHF is somewhat better than in those cases involving only one fluorine atom attached to a carbon atom. It is conceivable, then, that because of van der Waals repulsive forces, the C—F bond in a CF_2 group suffers some distortion relative to that in a

CHF group and therefore a different β_{C-F} should be used in the two cases. But this distortion, if it occurs, cannot be a lengthening of the C—F bonds for existing C—F bond length measurements in these molecules[18,21] reveal that, if anything, the C—F distance in CHF is longer than in CF_2—an observation supported by our bond-order calculations on CH_2CHF, CHFCHF, and CF_2CF_2 but *not* for CH_2CF_2.

Fortunately there is another possibility. In the CHF fragment, a strong C—F dipole is very near to a polarizable C—H bond. There should therefore be a charge separation induced in the latter resulting in additional negative charge flowing through the sigma bond on to the carbon atom. Thus we might expect an enhancement of the δq_1^{σ} term in Eq. 2. It can be shown (Table 4, column 2) that the induction of only 0·07e on to the carbon atom in molecules involving this group considerably improves the agreement with experiment.

Some support for this concept of induced charges is provided by the experimental difference in ionization potentials of the *cis* and *trans* difluoroethylenes. Indeed, this difference suggests that there is an induced C—H moment in the β C—H bonds as well. If this were not so, the *cis* and *trans* isomers should have the same ionization potential—a result observed for the *cis* and *trans* dimethyl ethylenes where no significant induced C—H moment would be expected. The 0·02 eV difference observed for the *cis* and *trans* dichloroethylenes, though barely outside experimental error, is in keeping with the above remarks. By analysing the experimental and calculated results in terms of induced C—H moments in the β positions as well, it is possible to achieve the agreement with experiment reported in column 3 of Table 4. Obviously there is a good deal of speculation involved in this analysis and it would be unwise to read too much into the calculations, particularly as the ω technique neglects all but nearest neighbour interactions. But they do indicate that it might be necessary in certain cases involving fluorine substitution to take account of possible "field" effects.

In Table 5 there are reported similar calculations on the chloro- and bromoethylenes. In these molecules there seems to be no need to include an induced C—H moment to obtain reasonable agreement with experiment. This is not surprising for the induced moments would not be expected to be large.

TABLE 5. THE IONIZATION POTENTIALS OF CHLORO-, BROMO-, AND FLUOROCHLOROETHYLENES

	X = Cl		X = Br				
	Expt.	Calc.	Expt.	Calc.		Expt.[22]	Calc.
CH_2CHX	9·995	10·06	9·80	9·93	c-CHFCHCl	9·86	9·92
CH_2CX_2	9·79	9·89	—	—	t-CHFCHCl	9·87	9·89
c-CHXCHX	9·65	(9·65)*	9·45	(9·46)*	c-CHFCFCl	9·86	9·93
t-CHXCHX	9·63	9·65	9·47	9·46	t-CHFCFCl	9·83	9·90
$CHXCX_2$	9·45	9·49	9·27	9·22			
CX_2CX_2	9·32	(9·32)*	—	—			

* expt. value used in deriving parameters

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[21] V. W. Laurie and D. T. Pence, *J. Chem. Soc.* **38**, 2693 (1963).

However, the measure of agreement reported in Table 5 was only achieved by allowing for some variation of β_{C-X}, for the CHX and CX_2 groups. There must almost certainly be strong van der Waals repulsions in the CCl_2 and CBr_2 fragments, not present in the CHCl and CHBr groupings, resulting in some distortion of the C—X bonds. Experimental evidence for this is rather meagre but microwave measurements[22] indicate 5% double bond character in CH_2CCl_2 but 7% in vinyl chloride. Consequently, we have varied β_{C-X} in the present calculations (Table 1 for numerical values).

It is gratifying to find that the above parameters for fluorine and chlorine substituents can successfully reproduce the observed ionization potentials for the *cis* and *trans* fluorochloroethylenes[23] given in Table 5. This suggests that our values have at least a certain internal consistency. This is especially evident when we remember how markedly the substitution of an additional fluorine atom into vinyl fluoride affects the ionization potential (e.g., from 10·37 eV down to 10·25 or 10·19 eV). But an additional fluorine substituent in *cis* and *trans* CHFCHCl has virtually no effect at all (0·04 eV)—a result reproduced by our calculations. This, and the possibility of field effects, should impress on us the difficulties associated with the interpretation of substituent effects in ethylenic systems.

(c) *Substituted methyl radicals.* One of the reasons for the present investigation was to check on the reliability of some of the electron-impact data in the literature concerning the ionization potentials of the fluoromethyl radicals. Electron-impact data on ionization potentials is, in general, much less reliable than that determined by photo-ionization techniques. But it is often the only convenient method of obtaining such data, particularly in the case of radicals. However, in the case of the trifluoromethyl radical, there is considerable disagreement amongst various experimentalists as to the "best" value; as a glance at the values in Table 6 shows. Included

TABLE 6. IONIZATION POTENTIALS OF SUBSTITUTED METHYL RADICALS

	Expt.*	Calc.
CH_3	9·843	(9·843)†
CH_2F	9·35	9·27
CHF_2	9·45	9·15
CF_3	10·10	
	9·35	
	9·3	9·17
	8·9	
CH_2Cl	9·32	9·24
$CHCl_2$	9·30	9·02
CCl_3	8·78 ± 0·05	
	<8·28 ± 0·15[28]	8·62
	>7·92 ± 0·35[28]	
$CFCl_2$	8·69 ± 0·15[28]	8·60

* unless otherwise indicated experimental values taken from Refs 4 and 15

† used in deriving parameters

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[22] S. Sekino and T. Nishikawa, *J. Phys. Soc. Japan* **12**, 43 (1957).

[23] J. Momigny, *Nature, Lond.* **199**, 1179 (1963).

in the Table are values calculated by us, assuming that both the radicals and ions were planar in their ground states. It now seems likely that the CF_3 radical is indeed pyramidal[24–26] so that the present calculations could be regarded as lower limits to the ionization potentials. These calculations were made using a $\beta_{\mathrm{C=F}}$ equal to that used in the fluorobenzene calculations.

As with the fluoroethylenes there is the possibility of induced C—H moments and the calculated values reported in column 2, Table 6 were arrived at with this in mind. It would seem that our present calculations rule out the possibility of the IP of CF_3 being as low as 8·9 eV. On the other hand it does not distinguish between the values around 9·3 eV and the much higher 10·10 eV value. However, Lossing *et al.*[27] have recently presented new evidence against the latter value. In view of all this it is our belief that reliable UV measurements are needed to settle this problem.

Similar considerations apply to the chloromethyl radicals, but our calculations do seem to rule out the low values of Curran.[28]

CONCLUSIONS

The main conclusions from this study seem to be:

(1) That the unusual trends associated with the successive substitution of fluorine into benzene and ethylene can be successfully calculated using the ω technique, provided that some attempt is made to include an inductive parameter for σ bonds.

(2) That the removal of the electron on ionization from the highest-occupied orbital of the parent molecule, particularly when the two highest oribitals have nearly equal energies, may not neccessarily lead to the most stable form of the ion. This may account for some of the difficulties associated with the divergence on successive iterations sometimes found in calculations employing the ω technique.[5,29]

(3) That in the fluorobenzenes, the differences in energy between possible ionic species are very small.

(4) That in order to describe successfully the behaviour associated with substituent effects in ethylenes, it may be necessary to consider "field" effects (especially for fluorine substitution) and the steric requirements of bulky substituents.

(5) That it is unlikely that the problems associated with the ionization of the fluoromethyl radicals will be settled without recourse to accurate UV measurements.

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[26] W. C. Price, T. R. Passmore and D. M. Roessler, *Disc. Faraday Soc.* **35**, 201 (1963).

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[28] R. K. Curran, *J. Chem. Phys.* **34**, 2007 (1961).

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