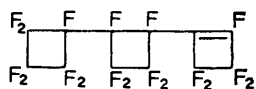


An ESCA Study of the Fluoride-ion-induced Trimerization Product from Perfluorocyclobutene

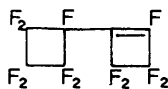
By David T. Clark,* Richard D. Chambers, and David B. Adams, Department of Chemistry, University of Durham, South Road, Durham City DH1 3LE

A study of the C_{1s} core electron spectra has been used to identify the structure of the product formed by the fluoride-ion-initiated trimerization of perfluorocyclobutene. Both an experimental approach, based on a comparison with compounds of known structure, and a theoretical approach, based on CNDO/2 SCFMO calculations and the charge potential model have been used. The structure indicated is different from two previously suggested.

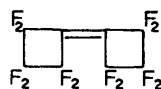
THE formation of a trimeric compound from perfluorocyclobutene was first reported in 1952; it was obtained



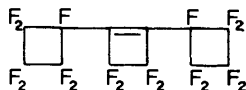
(I)



(II)



(III)



(IV)

when mixtures of perfluorocyclobutene and pyridine were set aside overnight.¹ The compound was tenta-

† To avoid confusion, roman numerals have been used throughout to denote the reaction products and possible structures of $C_{12}F_{18}$; arabic numerals have been reserved for model compounds for the interpretation of the C_{1s} spectrum of $C_{12}F_{18}$.

tively assigned structure (I)† on the basis of its chemical properties, which indicated the presence of a vinylic CF group. The fluoride-ion-initiated trimerization of perfluorocyclobutene was reported in 1965:² treatment of perfluorocyclobutene with fluoride ion yielded the dimers (II) and (III) together with a trimer $C_{12}F_{18}$ which was assigned structure (IV). Structural assignments were based largely on the method of synthesis and i.r. and n.m.r. data but in the case of the trimer were by no means unambiguous.

More recently Chambers and his co-workers³ have studied the fluoride-ion-initiated reactions of some perfluorocycloalkenes and have obtained the trimerization product of perfluorocyclobutene in good yield with only a trace of the dimerization products. However, structure (IV) previously assigned to this trimerization product was not in good agreement with the ^{19}F n.m.r. spectrum of Chambers' sample of the trimer.³ Consideration of the likely reaction mechanism for

¹ R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1638.

² M. J. R. Fraticelli, Ph.D. Thesis, Cornell University, 1965 (*Diss. Abs.*, 1965, **26**, 3045).

³ R. D. Chambers, M. Y. Gribble, and E. Marper, *J.C.S. Perkin I*, 1973, 1710.

trimer formation* suggests the four possibilities shown in Figure 1 and it was of interest to determine

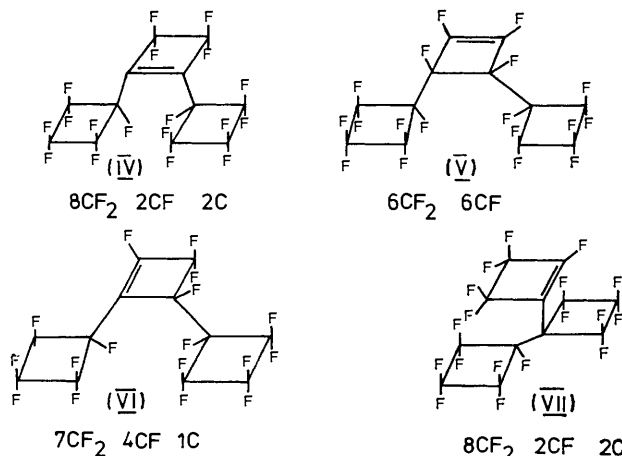


FIGURE 1 Possible structures of $C_{12}F_{18}$

whether ESCA could be used to differentiate between these. A detailed ESCA study has therefore been carried out on the trimer obtained in the fluoride-initiated reaction together with model systems to aid in the assignment of molecular core binding energies. Taken in conjunction with a parallel theoretical study based on the charge potential model, the data are only fully consistent with structure (VII). The analysis proceeds in two distinct steps: (a) an experimentally based identification; (b) a theoretical determination of the structure based on the charge potential model.

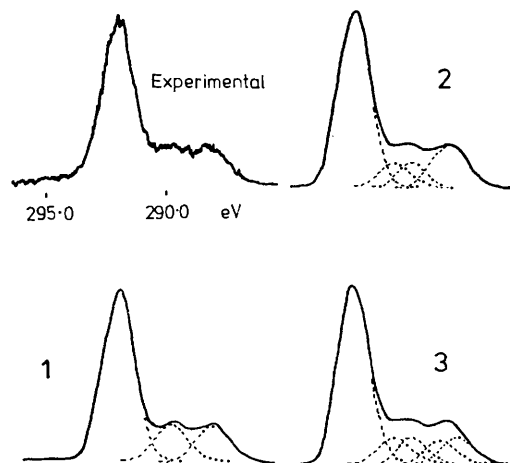


FIGURE 2 Experimental C_{1s} spectrum of $C_{12}F_{18}$ and deconvolutions into component peaks

(a) *Experimentally Based Identification.*—The C_{1s} ESCA spectrum of the trimer $C_{12}F_{18}$ was recorded (Figure 2), as were the C_{1s} ESCA spectra of four model

* The formation of dimer and trimer products may be rationalized in terms of a carbanion mechanism along the lines indicated in ref. 3. Such a mechanism leads straightforwardly to the possible trimer products discussed in the text. Interestingly, consideration of the likely stabilities of the equilibrating carbanionic species involved leads naturally to the conclusion that (VII) might well be the major product.

compounds (1)–(4). The spectra of compounds (3) and (4) have been reported and discussed previously.⁴ The trimer spectrum shows an overall $CF_2:CF:C$ ratio of 4:1:1 (*i.e.* 8:2:2). This immediately eliminates structure (I), and also (V) and (VI), which would show area ratios of 7:4:1, 6:6:0, and 7:4:1, respectively. Isomer (IV) has a high symmetry and therefore its C_{1s} spectrum would be expected to be resolved into $>CF_2$, $\geq CF$, and $>C=$ peaks. However, isomer (VII) has much less symmetry and contains $>CF_2$, $\geq CF$, $=CF-$, $>C=$, and $>C<$ bonding situations; hence its C_{1s} spectrum would be expected to have poorer resolution. The experimental spectrum is poorly resolved in the CF and C regions indicating that structure (VII) is more probable than structure (IV). Further analysis, in terms of the model compounds, was nevertheless required before a definite assignment could be made.

Three deconvolutions of the C_{1s} spectrum of the trimer were carried out by fitting gaussian curves in the area ratios 8:2:2, 8:1:1:2, and 8:1:1:1:1. The line-width at half maximum height for the C_{1s} peak was obtained from the well resolved C_{1s} spectra of compounds (1) and (2). (The CF_2 peak of the trimer was well resolved and consistent with the line-width obtained from the model compounds.) The deconvolutions correspond to three, four, and five distinct environments for the carbon atoms, respectively, and with the increased refinement of the deconvolutions the accuracy of the fit to the experimental spectrum increases. In fact the only deconvolution which is fully consistent with all the known data, *i.e.* line-widths, area ratios, and chemical shifts (see below), is the 8:1:1:1:1 deconvolution. The results of this series of deconvolutions are given in Table 2 and Figure 2.

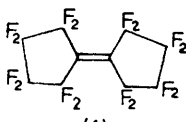
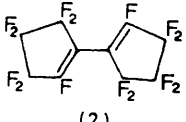
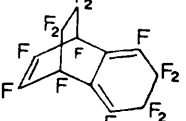
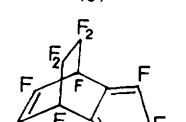
Deconvolution number 1, which would correspond to isomer (IV), gives a shift of 1.7 eV between the $>C=$ carbon atoms and the CF carbon atoms. Comparison with the model compounds (Table 1) shows that this internal shift is typical of a $=CF-$ carbon atom but not a $\geq CF$ carbon atom. Since there is no $=CF-$ bonding situation in isomer (IV), and also since a shift of 3.9 eV between $>C=$ and $>CF_2$ is a little low, this structure may be excluded. Deconvolution number 2 shows internal shifts of 3.9, 2.5, and 1.7 eV relative to the nonfluorinated carbon atoms; these shifts are fairly typical of $>CF$, $\geq CF$, and $=CF-$ carbon atoms and these carbon environments do occur in isomer (VII). The value of 3.9 eV for the internal shift between $>CF_2$ carbon atoms and a nonfluorinated carbon atom of the type $>C=$ is a little low, but isomer (VII) contains both a $>C=$ and a $>C<$ carbon atom and these may well have slightly different C_{1s} binding energies. Deconvolution number 3, area ratio 8:1:1:1:1, does in fact show an improved fit to the experimental spectrum and Table 2 lists internal shifts for both possible assignments of the $>C=$ and $>C<$ carbon atoms. Assign-

⁴ D. T. Clark, W. J. Feast, D. Kilcast, D. B. Adams, and W. E. Preston, *J. Fluorine Chem.*, 1972, **2**, 199.

ment (b) gives internal shifts which are not in agreement with any of the internal shifts expected on the basis of

TABLE 1

Binding energies and internal C_{1s} shifts in model fluoro-carbon compounds

Bonding environment	Binding energy	Internal shift
 (1)	>C=	0
	>CF ₂	4.1
 (2)	>C=	287.8
	=CF-	289.3
	>CF ₂	291.9
 (3)	>C=	287.8
	=CF-	299.4
	>CF	290.6
	>CF ₂	292.3
 (4)	>C=	288.0
	=CF-	289.6 ₅ (av.)
	>CF	290.9
	>CF ₂	292.3

For all model compounds the F_{1s} binding energies were 690.9 ± 0.1 eV

TABLE 2

Deconvolutions of the C_{1s} spectrum of $C_{12}F_{18}$

Area ratio	Binding energy † (eV)	Internal shift ‡ (eV)	Assignment
Deconvolution (1)			
2	288.1	0	>C=
2	289.8	1.7	>CF
8	292.0	3.9	CF ₂
Deconvolution (2)			
2	288.1	0	>C=
1	289.8	1.7	=CF-
1	290.6	2.5	>CF
8	292.0	3.9	CF ₂
Deconvolution (3) Assignment (a)			
1	287.9	0	>C=
1	288.6	0.7	>C-
1	289.8	1.9	=CF-
1	290.6	2.7	>CF
8	292.0	4.1	CF ₂
Assignment (b)			
1	287.9	-0.7	>C-
1	288.6	0.0	>C=
1	289.8	1.2	=CF-
1	290.6	2.0	>CF
8	292.0	3.4	CF ₂

† F_{1s} binding energy = 691.1 eV. ‡ Relative to >C=.

the model compounds and may therefore be rejected. Assignment (a), however, gives internal shifts which are in good agreement with those expected for isomer (VII). The trimer is therefore identified as isomer (VII).

TABLE 3

CNDO/2 Calculations on isomers (IV) and (VII)

Isomer	C atom no.	q_i	$\sum_{j \neq i} (q_j/r_{ij})$	$\frac{25q_i + \sum_{j \neq i} (q_j/r_{ij})}{(E - E^0)}$
Isomer (IV)	1	-0.0039	3.99	3.89
	2	0.3794	-2.03	7.46
	3	0.1384	2.27	5.72
	4	0.3293	-0.67	7.57
	5	0.3495	-1.07	7.65
	6	0.3483	-1.02	7.69
Isomer (VII)	1	-0.0325	4.47	3.66
	2	0.3833	-2.00	7.59
	3	0.1868	0.68	5.35
	4	0.3615	-1.58	7.46
	5	-0.0464	5.49	4.33
	6	0.3291	-0.60	7.63
	7	0.3772	-1.38	8.05
	8	0.3794	-1.52	7.96
	9	0.1496	2.44	6.18
	10	0.3321	-0.70	7.60
	11	0.3494	-0.93	7.75
	12	0.3472	-0.93	7.75

(b) *Theoretical Determination of Structure.*—As an alternative to the experimental approach, charges derived from CNDO/2 SCFMO calculations⁵ may be used in conjunction with the charge potential model⁶ to predict the spectra theoretically and the experimental and theoretical spectra can then be compared. [As previously noted, area ratio considerations alone dictate that only isomers (IV) and (VII) need be considered.] The relationship between charges and binding energies is given by equation (i), where the symbols have their

$$E = E^0 + \sum_i k q_i + \sum_{j \neq i} (q_j/r_{ij}) \quad (i)$$

usual meanings, and the values employed of $k_C = 25$ and $E^0_C = 284.6$ eV were those previously determined from a study of aromatic and perfluoroaromatic compounds.^{7,8} The charges and intramolecular Madelung potentials for the carbon atoms are listed in Table 3 and these were used to calculate the theoretical shifts, $E - E^0$. These shifts were then taken in conjunction with a line-width of 1.4 eV to obtain the experimental spectra for isomers (IV) and (VII). These are shown in Figure 3 together with the experimental spectrum normalised to a horizontal baseline. The experimental spectrum agrees closely with that calculated for isomer

⁵ J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

⁶ K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, 'ESCA Applied to Free Molecules,' North Holland, Amsterdam, 1969.

⁷ D. T. Clark and D. Kilcast, *J. Chem. Soc. (B)*, 1971, 2243.

⁸ D. T. Clark, D. B. Adams, and D. Kilcast, *Chem. Phys. Letters*, 1972, 13, 439.

(VII) but not with that for isomer (IV). This provides strong evidence that (VII) is the correct structure.†

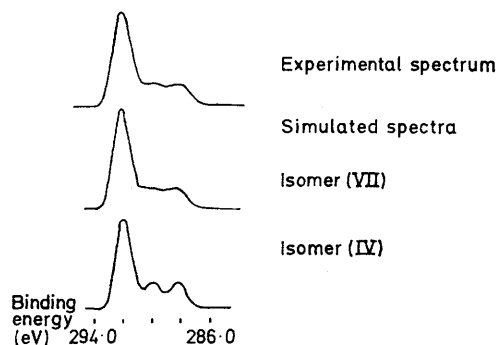


FIGURE 3

EXPERIMENTAL

The ESCA spectra were recorded as previously described^{7,8} and incompletely resolved spectra were decon-

volved with the aid of an analogue computer by standard procedures.⁹ The purity of the trimer was greater than 99% as evidenced by g.l.c. and from the detailed n.m.r. analyses following the work described in this paper.

Thanks are due to the S.R.C. for the provision of equipment and a research studentship (to D. B. A.).

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† The assignment of structure (VII) was in fact initially made on the basis of the ESCA study described here. Unfortunately ref. 3 does not present the structural assignment in chronological order (and in this sense is ambiguous) since it might appear that the original assignment was based on n.m.r. data and confirmed by ESCA, whereas the reverse was in fact the case. The initial ¹⁹F n.m.r. data did not allow a distinction to be drawn between (IV) and (VII) and it was only after the detailed ESCA study had shown that the data were only fully compatible with structure (VII) that further study located a vinylic CF group.

⁹ D. T. Clark, 'Chemical Aspects of ESCA, Electron Emission Spectroscopy,' ed. W. Dekeyser and D. Reidel, Dordrecht, Holland, 1973.