

THE CONSEQUENCES OF CATION RADICAL FLUORINATION THEORY—I

A COMPARISON OF VARIOUS THEORETICAL SCENARIOS WITH EXPERIMENT FOR CARBOCYCLIC-AROMATICS, USING CNDO/2 AND INDO CALCULATIONS

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Abstract—Various of the possible scenarios (Table 1) derived from cation radical fluorination theory are examined critically in the light of experiment. The predictions of the theory are made using CNDO/2 and some INDO calculations, and these are compared with the known experimental results for benzene, benzotrifluoride, naphthalene, anthracene and phenanthrene. It is concluded that cation radical theory must be broadly correct; it works well for monocyclic hydrocarbon compounds, assuming product control to be *via* spin or charge density in the intermediates (cations, radicals, cation-radicals), with sequence 3 (Table 1) preferred. In the absence of any modifying hypothesis, however, control of products by spin or charge density alone cannot explain the experimental results for the polycyclic substrates. The most plausible modifications appear to be product control via Wheland intermediate stability (sequence 7, Table 1) and/or rapid rearrangements.

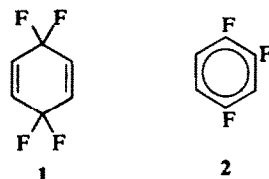
INTRODUCTION

We have proposed elsewhere¹ that fluorinations with high valency transition metal fluorides (HVMFs) are, like fluorinations with xenon trifluoride² and electrochemical fluorinations,³ oxidation processes which proceed via cation radical intermediates. Diagram 1, sequences 1 and 3, shows the types of reaction which we then proposed, with the initial fluorobenzene cation radical being formed by oxidative abstraction of an electron from fluorobenzene by, for example, Co^{3+} . We also proposed the use of molecular orbital calculations as predictive guides to the relevant properties of likely intermediates (cation radicals, cations, radicals) in these types of sequence.

Since then, another paper⁴ has appeared, taking up this idea and applying it to the fluorinations of hexafluorobenzene, pentafluoropyridine and sundry chlorofluoropyridines, but eschewing all discussion of the fluorination of hydrocarbons. This work⁴ suffers from two major weaknesses: first, rearrangements appear to occur rather readily in some of the systems studied, so that they cannot be easily ruled out in other cases; secondly, the authors did not actually know precisely which HVMF they were using.

This latter caveat might be thought to be academic in view of earlier suggestions^{1,5} that common pathways, and possibly mechanisms, are followed during the fluorinations of a given substrate over a range of HVMFs. Of late, however, it has become clear that the postulation of common predominant pathways must be abandoned, or at least substantially modified. To take the best documented examples, the fluorination of benzene over cobalt (III) fluoride (CoF_3) clearly proceeds almost entirely through the key intermediate 3,3,6,6-tetrafluorocyclohexa-1,4-diene (I),^{1,5,6} whereas fluorination of the same substrate over caesium tetrafluorocobaltate (III) (CsCoF_4) clearly goes, in substantial part, *via* the alternative intermediate 1,2,4-trifluorobenzene (II), and gives significant quantities of polyfluorobenzenes in the product mixture.⁷ Diene (I) has been isolated from CoF_3 ,⁵ KCoF_4 ,⁸ and LiCoF_4 ,⁹

product mixtures, and with the latter it may even form the major part of the product. Fluorination of diene (I) over CsCoF_4 ,⁹ however, does not give the same products as does the fluorination of benzene, and therefore this diene does not react to yield 1,2,4-trifluorobenzene (see later) under the usual fluorination conditions over this reagent.



The fluorinations of tetrahydrofuran over CoF_3 ,¹⁰ and KCoF_4 ,¹¹ provide another compelling dichotomy of mechanism.

It is thus now well established that different HVMFs can give different major fluorination pathways with the same substrate, and hence any theory which attempts to rationalise these pathways must offer some explanation of this variation. This is separate from the question of how far along a particular pathway a given HVMF can take a substrate—this depends mainly on the oxidation potential of the transition metal in the HVMF (e.g. Co^{3+} in CoF_3).¹

The present paper now gives the first attempt to set out and evaluate, for aromatic hydrocarbons, the various fluorination mechanisms that might be imagined to flow from the oxidation¹—and hence cation radical^{1,4}—theory of fluorination. In this first instance this has been done for some carbocyclic substrates for which experimental fluorination results are available; we shall present our results for heterocycles in a subsequent publication.

The initial electron abstraction to form the cation radical may, of course, lead to a number of different consequences, and those discussed in this paper are listed in Table 1. It should be said at the outset that only kinetic products are to be considered here. We hope to discuss possible thermodynamic factors in a later publication.

Table 1. Some possible sequences deriving from the cation radical postulate

Sequence No.	1st Step governed by	Product type	2nd Step (governed by)	Product type	3rd Step (governed by)	Product type	Example sequences	
1	charge	ArFH [•]	Add F ⁻ (spin)	→	→	Adduct e.g. 1,4-diene		
2	charge	ArFH [•]	Lose H [•]	→	→	Aromatic		
3	charge	ArFH [•]	Lose e ⁻	ArFH ⁺	Add F ⁻ (charge)	Adduct		
4	charge	ArFH [•]	Lose e ⁻	ArFH ⁺	Lose H ⁺	Aromatic		
5	spin	ArFH [•]	Add F ⁻ (charge)	→	→	Adduct		
6	spin	ArFH [•]	Lose H [•]	→	→	Aromatic		
7*	Position of the initial attack is controlled by the stability of the cationic Wheland intermediate formed by addition of F ⁻							
8*	Position of the initial attack is controlled by the stability of the radical Wheland intermediate formed by addition of F ⁻							

* Each of these may be followed by a variety of quenching or H abstraction sequences (similar to 1-6) not separately detailed here.

The object of the present paper should now be clear; it is to predict the products which would be formed from a consistent following of each sequence in Table 1, and to compare them with experiment in the hope that this will afford some insight into the finer detail of the fluorination process.

METHOD AND RESULTS

Before the programme can be implemented a means must be found to make the predictions. We have estimated the energies of, and charge and spin densities in, the various intermediates using molecular orbital calculations in the CNDO/2¹² approximation, since these are readily carried out and can be expected to give *correct ranking orders* for the various properties of the intermediate cations, radicals and cation radicals of interest. This expectation is quite reasonable, although the absolute values of these properties (energies, densities) may well be in some error. As a check, several calculations have been performed also in the INDO¹³ formulation, which is known to give more reliable spin population analyses. Such calculations were found to produce the same rank order of electronic populations, and hence to predict the same positions of attack as did the CNDO/2 calculations.

The CNDO/2 program used is a version of QCPE 91, modified to run on an ICL 1906A machine under GEORGE 3. We thank Dr. D. W. Davies and his collaborators for permission to use this program.

No serious attempts have been made to optimise the geometries used for the calculations, because our experience with preliminary studies in this area has been that electron densities and spin densities are but little affected by *small* changes in geometry—always provided that the geometries are not wholly unreasonable—although the calculated energies are, of course, strongly affected. It must be said however, that it is possible to “force” a position of highest charge or spin density by an injudicious choice of geometry,¹⁴ and that this hazard must be borne in mind.

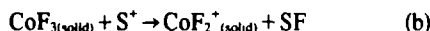
The actual geometries used are as follows. For the benzenes, and molecules derived therefrom, a regularly hexagonal carbon skeleton was used, with C-C = 1.40 Å, C-F = 1.33 Å and C-H = 1.08 Å. Saturated (tetrahedral) carbons had C-F = 1.36 Å and C-H = 1.09 Å, with the ring plane bisecting the tetrahedral angle. In the case of the benzotrifluorides, the CF₃ group had one fluorine on one side of the ring and two fluorines symmetrically placed upon the other: for this grouping C-C = 1.52 Å and C-F = 1.36 Å. These bond lengths are standard ones taken from Pople and Beveridge's monograph.¹⁵ For naphthalenes, anthracenes and phenanthrenes, experimental carbon skeletons¹⁶ were used, with the other parameters as for the benzenes, and C-H or C-F bonds bisecting the relevant C-C-C angles.

The results of the various calculations are set forth in Tables 2-6. These tables are rather indigestible, and so diagrams 1-4 have been constructed from them. These diagrams do not show all the detail, since this would render them all but unintelligible. The diagrams show the pathways predicted by the various fluorination sequences in Table 1, excepting that some of these sequences, whilst quite possible, are not discussed at length here. This is explained later in the discussion.

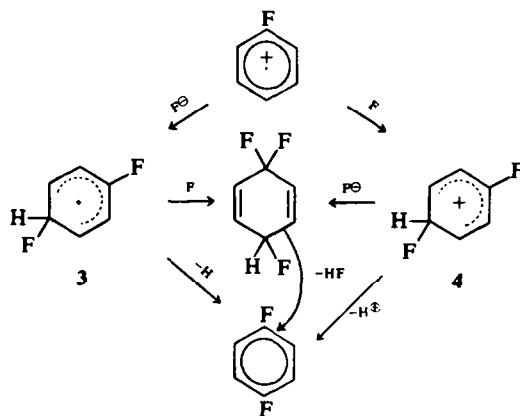
DISCUSSION

It will be convenient to reiterate here the main features of the processes under examination. Broadly, it is

assumed that in the HVMF fluorination of aromatics the first step is the abstraction of an electron from the π system, and that the cation radical thus (formally) formed has a sufficiently long lifetime for its properties to govern the position of fastest attack—by either F⁻ or F[•]—upon it. Naturally, we do not suppose that there are free fluorine atoms in the fluorination reactors, or even free fluoride ions: these representations are used only as shorthand forms. We really suppose that, for example, over CoF₃, reactions like (a) or (b) are proceeding (S = substrate molecule); it is also possible that S[•] and S⁺ are not completely free, but are bound in some way to the cobalt fluoride lattice.⁴



Once the cation radical has been quenched, the species so formed may then acquire either F⁻ or F[•] to make a closed shell molecule (Scheme 1); this second step will naturally be expected to be fastest at the position of highest charge or spin density, as appropriate.



Scheme 1.

Alternatively, the second step may be the loss of H[•] or H⁺ to give an aromatic system. A further possibility is that the position of attack by F⁻ or F[•] on a radical cation may be controlled by the relative stabilities of the Wheland-type intermediates (e.g. 3, 4 and their *o* and *m* isomers) which may form. Fluorination pathways may therefore be predicted by considering charge or spin density in, or energy of, the various intermediates.

Of course, only the major pathways can be thus delineated; minor by-ways cannot be ruled out, and it is also very difficult to make quantitative estimates of the relative importances of different routes. This latter difficulty is especially severe in the sequences where spin is a dominating feature, since the energetics of this are obscure.

Hopefully, when the prediction of favoured routes is compared with experiment the possible sequences will be narrowed down to one, for a particular substrate and HVMF. Such a choice would, of course, be particularly attractive if the same sequence emerged for several substrate/HVMF pairs.

There is an obvious possibility which we have thus far neglected: direct transfer of a fluorine ligand from the HVMF to the substrate:

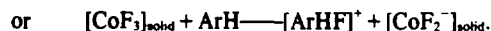
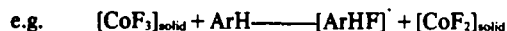



Table 2. Calculated spin, charge densities and energies for intermediates in the fluorination pathways for benzene

Numbering as in:  CH = +ve charge density
S = spin density



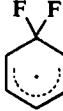

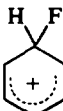



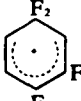

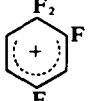
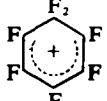

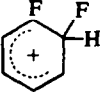
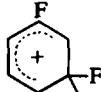

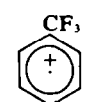
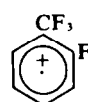
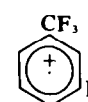
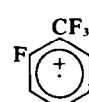

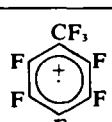
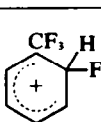
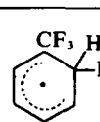
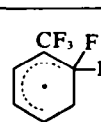
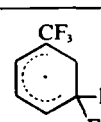
Posn. No.				
	S CH	S F CH	S	CH
1	0.282 0.380	0.285 0.367	-0.063	0.399
2	0.114 0.015	0.051 0.013	-0.407	0.120
3	-0.011 0.045		-0.186	-0.032
4	0.355 0.158		0.432	0.230
5				
6				
Posn. No.				
	CH	CH	S	S CH
1	0.186	0.399	-0.060	0.229 0.371
2	0.135	0.118	0.390	-0.065 -0.095
3	-0.075	-0.073	-0.180	0.154 0.305
4	0.421	0.450	0.412	0.312 0.321
5	Energy =			-0.045 -0.007
6	101.4698 a.u.			0.167 0.040
Posn. No.				
	S	CH	CH	CH
1	-0.060	0.408	0.370	0.352
2	0.379	0.046	0.363	0.292
3	-0.170	0.174	-0.139	0.127
4	0.424	0.413	0.449	0.365
5	-0.186	-0.068	-0.068	
6	0.401	-0.123	-0.101	
Posn. No.				
	S			
1	-0.060			
2	0.388			
3	-0.195			
4	0.408			
5				
6				
	Energy =	Energy =		
	101.4646 a.u.	101.4484 a.u.		

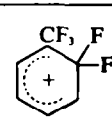
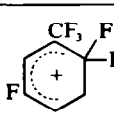
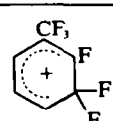
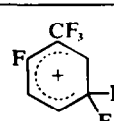
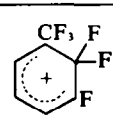
Table 3. Calculated spin, charge densities and energies for intermediates in the fluorination pathways for benzotrifluoride

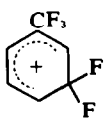
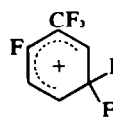
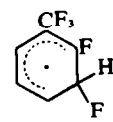
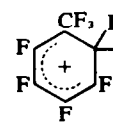
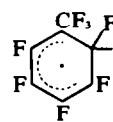
Numbering as in: 

Posn. No.										
	CH	S	CH	S	CH	S	CH	S	CH	S
1	0.02	0.141	-0.041	0.143	0.037	0.119	-0.028	0.054	-0.083	-0.074
2	0.08	0.072	0.325	0.116	0.006	0.060	0.024	0.052	0.333	0.370
3	0.05	0.076	-0.004	0.073	0.307	0.101	0.365	0.280	0.322	0.264
4	0.04	0.002	0.071	0.008	-0.010	0.026	0.020	0.052	-0.035	-0.078
5			0.050	0.081	0.064	0.056	0.012	0.045	0.139	0.197
6			0.071	0.035	0.066	0.091	0.379	0.281	0.132	0.201

Posn. No.						
	CH	S	CH	S	S	S
1	-0.137	-0.078	0.075	0.381	0.391	-0.181
2	0.343	0.213	0.195	-0.088	-0.064	0.413
3	0.263	0.240	0.134	0.382	0.402	-0.065
4	0.174	-0.104	-0.026	-0.176	-0.184	0.405
5			0.194	0.390	0.422	-0.186
6			-0.102	-0.176	-0.178	0.430

Energy = 164.1353 a.u.

Posn. No.					
	CH	CH	CH	CH	CH
1	0.068	0.063	-0.131	-0.114	0.048
2	0.408	0.406	0.376	0.135	0.381
3	0.122	0.118	0.369	0.396	0.367
4	-0.029	-0.069	0.103	0.126	-0.088
5	0.227	0.449	-0.028	-0.075	0.221
6	-0.016	-0.055	0.240	0.458	-0.012

Posn. No.					
	CH	CH	S	CH	S
1	-0.074	-0.116	-0.178	-0.021	-0.338
2	0.134	0.151	0.371	0.394	-0.059
3	0.395	0.182	-0.087	0.315	0.404
4	0.127	0.142	0.389	0.126	-0.194
5	-0.033	-0.076	-0.181	0.367	0.406
6	0.241	0.431	0.400	0.205	-0.146

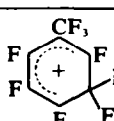
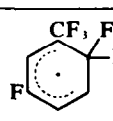
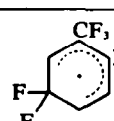
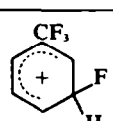
Posn. No.				
	CH	S	S	CH
1	-0.165	0.378	-0.174	
2	0.366	-0.060	0.405	

Table 3 (Contd)

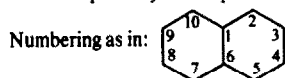
3	0.344	0.379	-0.178	
4	0.298	-0.178	0.381	
5	0.115	0.399	-0.061	
6	0.422	-0.168	0.402	Energy = 164.1353 a.u.



1
2
3
4
5
6

Energy = 164.1342 a.u.

Table 4. Calculated spin, charge densities and energies for intermediates in the fluorination pathways for naphthalene



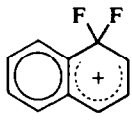
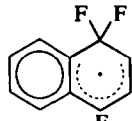
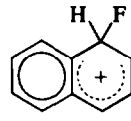
Posn. No.						
	CH	S	CH	S	CH	S
1	0.010	-0.052	-0.020	-0.034	0.035	-0.038
2	0.104	0.221	0.338	0.213	0.035	0.249
3	0.048	0.055	0.000	0.106	0.337	0.160
4			0.053	0.032	-0.058	-0.056
5			0.104	0.266	0.117	0.182
6			0.027	-0.061	0.019	0.001
7			0.079	0.177	0.072	0.117
8			0.044	0.021	0.086	0.161
9			0.049	0.067	0.015	-0.048
10			0.091	0.151	0.091	0.215

Posn. No.						
	CH	S	CH	S	CH	S
1	-0.006	-0.042	-0.065	-0.037	0.019	0.086
2	0.331	0.237	0.394	0.158	0.485	0.117
3	0.006	0.079	-0.003	0.110	-0.014	0.038
4			0.036	0.011		
5			0.081	0.230		
6			0.041	-0.070		
7						
8						
9	0.047	0.036			0.038	0.017
10	0.049	0.128			0.072	0.078

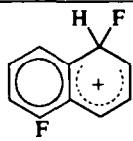
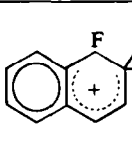
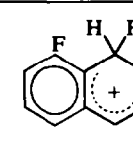
Posn. No.			
	CH	S	CH
1	0.041	0.137	0.073
2	0.399	-0.052	0.179

Table 4 (Contd)

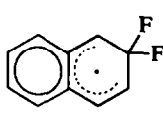
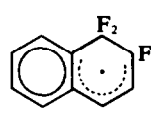
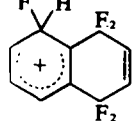
3	0.149	0.542	0.169
4	-0.045	-0.192	-0.097
5	0.213	0.424	0.407
6	-0.010	-0.092	-0.042
7	0.064	0.089	0.063
8	0.007	-0.057	0.007
9	0.087	0.101	0.079
10	0.013	-0.057	-0.004

		
CH	S	CH

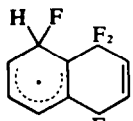
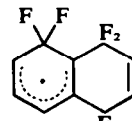
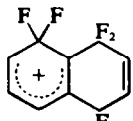
1	0.039	0.128	0.064
2	0.384	-0.059	0.144
3	0.148	0.516	0.404
4	-0.086	-0.185	-0.104
5	0.425	0.400	0.185
6	-0.050	-0.087	-0.012
7	0.072	0.083	0.050
8	0.014	-0.053	0.011
9	0.090	0.094	0.073
10	0.018	-0.052	0.002

		
CH	CH	CH

1	0.082	-0.051	0.019
2	0.182	0.397	0.192
3	0.168	0.163	0.173
4	-0.049	0.023	-0.046
5	0.199	-0.007	0.186
6	-0.048	0.135	0.009
7	0.284	-0.023	0.035
8	-0.055	0.102	0.025
9	0.096	-0.002	0.017
10	0.021	0.074	0.228

		
S	S	CH

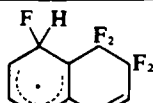
1	-0.142	0.124	0.080
2	0.618	-0.059	0.428
3	-0.059	0.513	-0.037
4	0.146	-0.193	-0.027
5	-0.085	0.392	0.433
6	0.224	-0.084	-0.043
7	-0.101	0.080	0.189
8	0.171	-0.050	-0.031
9	-0.099	0.090	0.158
10	0.148	-0.050	0.181

		
S	S	CH

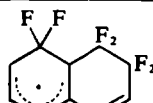
1	0.330	0.338	0.072
2	-0.014	-0.019	0.429
3	0.003	0.004	-0.038

Table 4 (Contd)

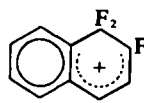
4	-0.003	-0.004	-0.026
5	0.007	0.008	0.433
6	-0.170	-0.170	-0.040
7	0.358	0.382	0.183
8	-0.182	-0.189	-0.027
9	0.454	0.472	0.147
10	0.100	-0.082	0.191



S

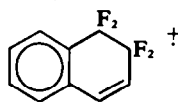


S



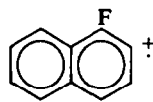
CH

1	0.341	0.348	0.034
2	-0.020	-0.023	0.354
3	0.004	0.004	0.393
4	-0.088	-0.087	-0.104
5	0.052	0.052	0.204
6	-0.163	-0.164	-0.010
7	0.355	0.388	0.058
8	-0.182	-0.193	0.014
9	0.452	0.481	0.075
10	-0.108	-0.083	0.023



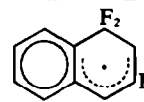
CH

S



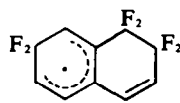
CH

S

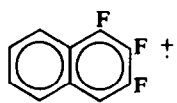


S

1	-0.010	0.085	-0.016	-0.051	0.136
2	0.469	0.180	0.319	0.183	-0.049
3	0.457	0.131	-0.006	0.063	0.507
4	-0.083	0.013	0.063	0.054	-0.182
5	0.076	0.039	0.095	0.205	0.428
6	0.054	0.028			-0.092
7	0.030	0.027			0.089
8	0.045	0.006			-0.057
9	0.031	0.012			0.101
10	0.075	0.070			-0.056

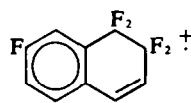


S



CH

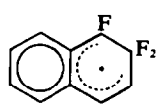
S



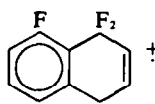
CH

S

1	-0.193	-0.004	-0.042	0.008	0.075
2	0.009	0.291	0.251	0.472	0.190
3	0.014	0.199	0.045	0.463	0.139
4	0.285			-0.094	0.018
5	-0.149			0.084	0.034
6	0.398			0.028	0.026
7	-0.144	0.079	0.132	0.050	0.022
8	0.279	0.047	0.037	-0.015	0.002
9	-0.056			0.280	0.010
10	0.405			-0.002	0.056



S



CH

S

1	-0.137	-0.013	0.087
2	0.587	0.503	0.107
3	-0.055	-0.020	0.035
4	0.132		

Table 4 (Contd)

5	-0.075					
6	0.205					
7	-0.091					
8	0.155					
9	-0.091	-0.003	0.021			
10	0.137	0.290	0.077			

	CH	S	CH	S	CH	S
1	-0.043	0.096	-0.015	-0.051	0.005	-0.059
2	0.489	0.114	0.281	0.255	0.276	0.282
3	-0.023	0.041	0.287	0.184	0.292	0.135
4	-0.008	0.029	-0.045	-0.059	-0.095	0.015
5	0.478	0.105	0.116	0.219	0.344	0.196
6	0.035	0.076	0.028	-0.022	-0.009	-0.1010
7	0.056	0.071	0.062	0.109	0.068	0.092
8	0.067	0.015	0.068	0.086	0.057	0.080
9	-0.014	0.027	0.029	-0.007	0.036	0.008
10	0.308	0.090	0.084	0.159	0.076	0.146

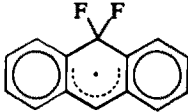
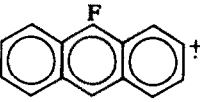
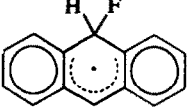
	CH	S	CH	S	CH	S
1	-0.067	0.090	0.068		0.139	
2	0.458	0.165	0.188		-0.084	
3	0.449	0.117	0.169		0.524	
4	-0.070	0.011	-0.049		-0.188	
5	0.070	0.043	0.189		0.399	
6	0.079	0.031	-0.008		-0.091	
7	0.018	0.030	0.052		0.083	
8	0.071	0.007	0.007		-0.057	
9	-0.026	0.021	0.079		0.095	
10	0.311	0.083	-0.005		-0.059	

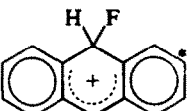
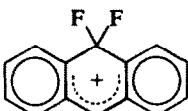
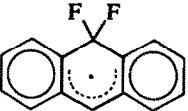
Table 5. Calculated spin, charge densities and energies for intermediates in the fluorination pathways for anthracene

Numbering as in:

Posn. No.						
	CH	S	S	CH	CH	S
1	0.108	0.273	-0.048		0.411	
2	0.023	-0.034	0.216		0.044	
3	0.050	0.112	-0.093		0.007	
4	0.039	0.036	0.155		0.099	
5			-0.088		0.001	
6			0.139		0.072	
7			-0.125		-0.026	
8			0.504		0.204	
9						
10						
11						
12						
13						
14						

Table 5 (Contd)

			
	S	CH S	S
1	-0.031	0.323	0.227
2	0.211	-0.024	-0.009
3	-0.089	0.058	0.085
4	0.158	0.041	0.953
5	-0.087	0.046	0.014
6	0.143	0.045	0.118
7	-0.125	0.032	-0.049
8	0.516	0.088	0.303
9			
10			
11			
12			
13			
14			

			
	CH	CH	S
1	0.206	0.413	-0.029
2	0.087	0.054	0.202
3	-0.017	0.007	-0.085
4	0.092	0.089	0.150
5	-0.007	-0.002	-0.083
6	0.064	0.079	0.136
7	-0.024	-0.056	-0.121
8	0.193	0.416	0.494
9			
10			
11			
12			
13			
14			

*dissymetrised here for convergence

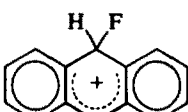
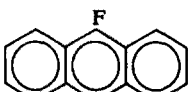
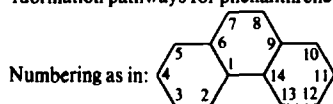
		
	CH	CH S
1	0.201	0.311 0.256
2	0.082	-0.003 -0.025
3	-0.012	0.052 0.092
4	0.094	0.039 0.032
5	-0.002	
6	0.074	
7	-0.067	
8	0.401	
9		
10		
11		
12		
13		
14		

Table 6. Calculated spin, charge densities and energies for intermediates in the fluorination pathways for phenanthrene



Posn. No.						
	CH	S	CH	S	CH	S
1	0.062	0.136	0.050	0.084	0.058	0.079
2	0.008	0.034	0.009	-0.015	-0.011	-0.036
3	0.036	0.033	0.087	0.201	0.069	0.125
4	0.032	0.002	0.000	-0.077	0.010	-0.048
5	0.029	0.089	0.051	0.178	0.028	0.099
6	0.058	0.058	0.060	0.024	0.033	0.005
7	0.038	0.054	0.006	0.182	0.081	0.137
8			0.334	0.158	0.062	0.105
9			-0.026	-0.025	0.008	0.040
10			0.059	0.127	0.315	0.215
11			0.004	-0.044	-0.051	-0.027
12			0.068	0.108	0.089	0.128
12			0.007	0.016	0.050	0.148
14			0.059	0.029	0.026	-0.030

Posn. No.						
	CH	S	CH	S	S	F
1	0.098	0.133	0.068	0.066	-0.026	
2	-0.006	0.016	-0.029	-0.037	0.029	
3	0.037	0.039	0.054	0.076	-0.021	
4	0.024	0.001	0.019	-0.020	0.027	
5	0.010	0.061	0.010	0.043	-0.024	
6	0.063	0.075	0.037	0.020	0.042	
7	0.024	0.018	0.072	0.075	-0.039	
8	-0.037	0.067	0.036	0.073	0.038	
9	0.070	0.041	0.029	0.016	-0.088	
10	-0.003	0.074	0.316	0.273	0.479	
11	0.043	0.005	-0.021	-0.005	-0.193	
12	-0.038	0.037	0.021	0.148	0.513	
13	0.275	0.073	0.318	0.190	-0.050	
14	0.026	0.124	-0.038	-0.051	0.165	

Posn. No.						
	CH	S	S	CH	CH	S
1	0.032		0.050		0.065	
2	0.002		-0.032		-0.021	
3	0.015		0.036		0.044	
4	0.046		0.025		0.014	
5	-0.018		0.034		0.011	
6	0.065		-0.037		0.013	
7	0.024		0.118		0.003	
8	0.021		-0.058		-0.009	
9	0.002		0.215		0.086	
10	0.213		-0.048		0.393	
11	-0.039		0.448		0.101	
12	0.136		-0.188		-0.039	
13	0.399		0.462		0.202	
14	0.029		-0.120		-0.029	

Table 6 (Contd)

	S	CH	S
1	0.199	0.127	-0.079
2	-0.110	-0.040	0.280
3	0.190	0.129	-0.145
4	-0.094	-0.009	0.286
5	0.181	0.075	-0.191
6	-0.132	-0.020	0.408
7	0.616	0.186	-0.115
8	-0.060	0.396	0.223
9	0.039	-0.024	-0.051
10	-0.019	0.019	0.059
11	0.025	0.041	-0.033
12	-0.018	0.023	0.062
13	0.029	0.018	-0.041
14	-0.029	0.008	0.077

	CH
1	0.178
2	0.055
3	-0.022
4	0.143
5	-0.072
6	0.189
7	-0.051
8	0.140
9	0.003
10	0.025
11	0.013
12	0.048
13	-0.006
14	0.036

We shall not explicitly consider this as a separate possibility, since it is difficult to see how it could lead to any great selectivity in fluorination, which is required in several cases,^{9,11} unless the position of attack was governed by the stability of the Wheland-type intermediate formed. This process thus forms sub-sets of sequences 7 and 8 in Table 1, and need not be separately considered. If such a process were important it would, of course, exclude cation radicals from the fluorination pathway: this is not a point against the ligand transfer processes, however, since the real transition state for initial fluorine attack on a cation radical must bear *some* resemblance to a direct ligand transfer, with a fluorine atom bonded partially to the HVMF lattice and partly to the substrate. The point at issue is whether this transition state is best described in terms of attack on a cation radical (leading to attack controlled by spin or charge density) or in terms of ligand transfer (leading either to a substantially random attack or to control by Wheland intermediate stability).

Because of likely lack of selectivity (radical attacks on benzenoid aromatics are usually rather unselective processes) we also dismiss sequence 8 in Table 1 from further consideration.

This last preliminary comment concerns sequences 2, 4 and 6 in Table 1. These lead to very much the same products as 1, 3 and 5 respectively, and only seriously differ from them in the very early stages, when only one or two fluorines have been introduced. Indeed, it is quite possible that monofluorobenzene and *p*-difluorobenzene are formed by sequence 4, say, and that sequence 3 then takes over because reversion to an aromatic is no longer possible (see sequence 3, diagram 1): one small piece of evidence against 2, 4 or 6 and in favour of 1, 3 or 5 is the isolation, in very low yield, of an isomer of $C_6F_6H_6$ from the $KCoF_4$ fluorination of benzene.⁸ Generally, therefore, sequences 2, 4 and 6 will not be discussed at length, although we recognise that they may usually replace 1, 3 or 5, respectively, in the early stages of a fluorination.

It thus remains to examine sequences 1, 3, 5 and 7 to see which, if any, of them can plausibly explain the product distributions observed from HVMF fluorinations. Clearly, since different HVMFs sometimes give different predominant products, there will probably not be only a single general pathway. Even over a single HVMF many products (~ 30 from $C_6H_6 + CoF_3$)^{5,6} are commonly isolated, and so we may hope, even here, only to sketch in the major pathway, not all the by-ways.

In all our calculations on cations and cation radicals, the position of highest positive charge density is invariably a carbon atom bearing a fluorine, if there is one in the conjugated system; spin densities do not show a similar preference.

Benzene. From the calculated spin and charge densities (Table 2) it is possible to construct the fluorination paths shown in digram 1 for sequences 1, 3 and 5. The pathway for sequence 7 follows from the calculated energies (Table 2) of the Wheland intermediates and from the orientation of nitration¹⁸ in the various polyfluorobenzenes.

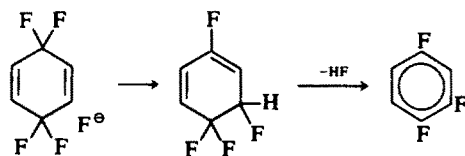
These sequences are straightforward in that it is only in sequence 1 that any appreciable branching of the main pathway is likely; sequences 3 and 5 predict only diene (1) as a major product, and sequence 7 predicts a series of polyfluoroaromatics. It is difficult to estimate the relative importances of the main and side routes in sequence 1 since the separating factor is spin; it is, however, clear that, as in sequences 3 and 5, diene (1) is the predicted major product with 1,3,3,6,6-pentafluorocyclohexa-1,4-diene (5) as the next most important. We eschew here and later any detailed discussion of the subsequent fate of the dienes—unless they may dehydrofluorinate directly to an aromatic—since their fluorinations present no features currently of interest.

Chambers *et al.*⁴ have presented the case against sequence 7; we agree with their general reservations, although we feel that it is not impossible that the stabilisation of the cation radical intermediates by interaction with the crystal lattice (acting as a "solid solvent"), an effect discussed by these workers, is less than the corresponding stabilisation for cationic Wheland intermediates, so that the actual energetics of the overall situation may not be quite as envisaged by Chambers *et al.* In particular, it may be that the energies of the cationic and cation radical intermediates, together with their associated inorganic species, may be very comparable; thus the primacy of the cation radical as product determining intermediate is not wholly certain. We hope, however, to show that sequence 7 can be ruled out on experimental grounds as well as theoretical ones.

These predictions must now be compared with experiment. For fluorinations of benzene over CoF_3 ,^{5,6} all the compounds predicted in sequences 1, 3 and 5 have been isolated, as have numerous compounds derived from these by saturation of double-bonds with fluorine; only a few of the polyfluoroaromatics predicted by sequence 7 have been isolated, and these in very low yield.^{5,6} Bearing in mind the earlier comment that only the major pathways can be sketched in by a survey of this sort, we therefore note that the product distributions from low temperature fluorinations with this reagent^{5,6} heavily favour 1 against 2 as the key intermediate. Of course, higher temperature ($\geq 250^\circ$) fluorinations give mostly saturated products⁶ with but little hydrogen left, but even here the products have been rationalised as arising principally from 1. Thus, although the evidence is not wholly conclusive, it seems clear that 1 is the key intermediate over CoF_3 .

Even more strikingly, the recently discovered reagent LiCoF_4 gives, under suitable conditions, high yields of 1 in its product mixtures from benzene; indeed, at low temperatures (100–130°) this is virtually the sole product. Thus, 1 must be the preferred intermediate in fluorinations of benzene with this reagent, as it must with the better known potassium salt (KCoF_4).⁸ The caesium⁷ salt of this series gives unusually high percentages of highly fluori-

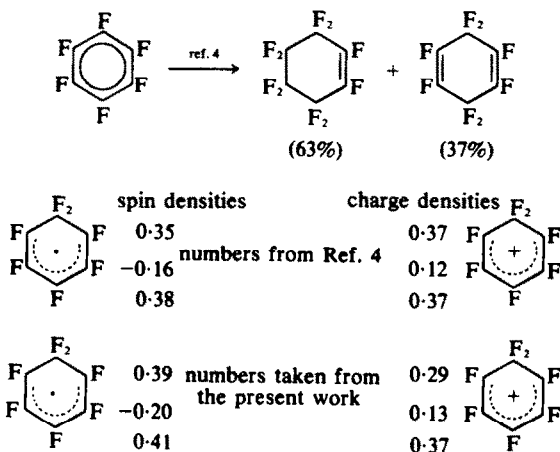
nated aromatics in the product mixture, but 1 is still the major product and must thus be an important compound in fluorinations with this reagent also. It is very noteworthy that 1 does not fluorinate over CsCoF_4 to give polyfluorobenzenes,⁹ so that the easily conceived rearrangement/dehydrofluorination sequence leading from 1 to 2 (Scheme 2) does not occur under fluorination conditions, at least over this reagent. Thus, the only sequence which can rationalise the large quantities of polyfluoroaromatics⁷ in the CsCoF_4 fluorination of benzene is sequence 7.



Scheme 2.

Taken together, these data militate against a single sequence being followed by all the HVMFs. If we regard CoF_3 , LiCoF_4 and KCoF_4 as being at one end of a spectrum of reactivities, with CsCoF_4 at the other, then we can say certainly that sequences 3 and 5 are excluded as the *only* major routes for CsCoF_4 , whilst these are the best two sequences for the other three reagents. Similarly, sequence 7 is excluded for CoF_3 , LiCoF_4 and KCoF_4 , but seems to fit *some* of the CsCoF_4 products best. Sequence 1 cannot convincingly explain the CsCoF_4 results, since the route to the polyfluoroaromatics—as opposed to 1,4-dienes—lies always along the less favoured forks in the route: it also seems to have too many branches to be satisfactory for LiCoF_4 and KCoF_4 , although it could apply over CoF_3 .

The results and comments of Chambers *et al.* might be germane here: they have considered the fluorination of hexafluorobenzene over what may be $\text{Ca}(\text{CoF}_4)_2$, and obtained the products shown in Scheme 3.

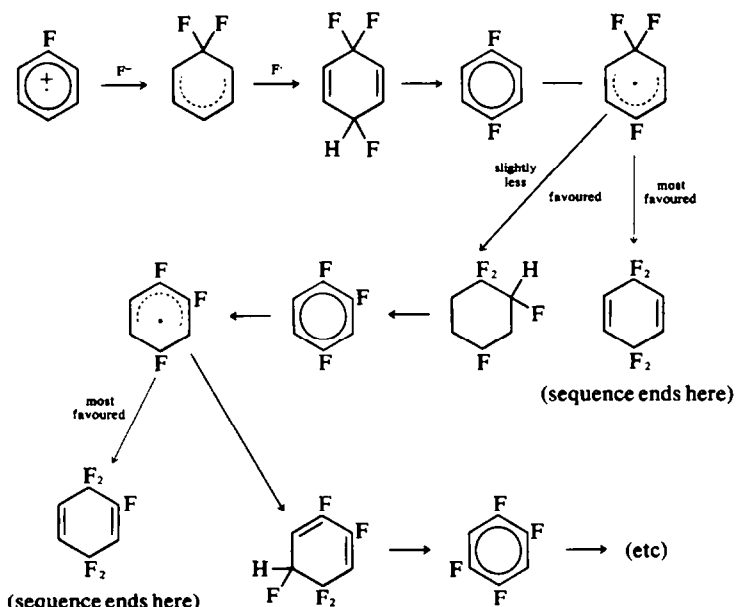


Scheme 3.

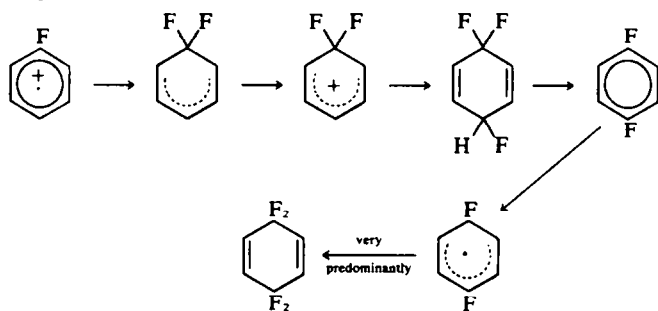
These authors have opted for sequence 1 in their case, arguing from their calculated charge and spin densities in the relevant Wheland intermediates (Scheme 3). They found that the spin densities in radical intermediate favoured *para* attack, whereas the charge densities in the cationic intermediate did not distinguish between the

Diagram 1 Predicted Fluorination Pathways for Benzene†

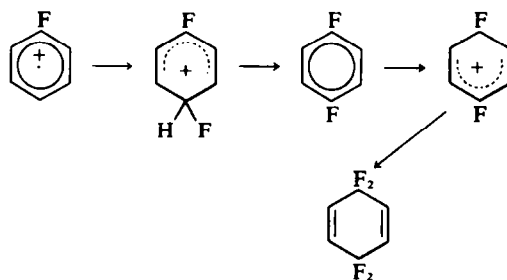
Sequence 1



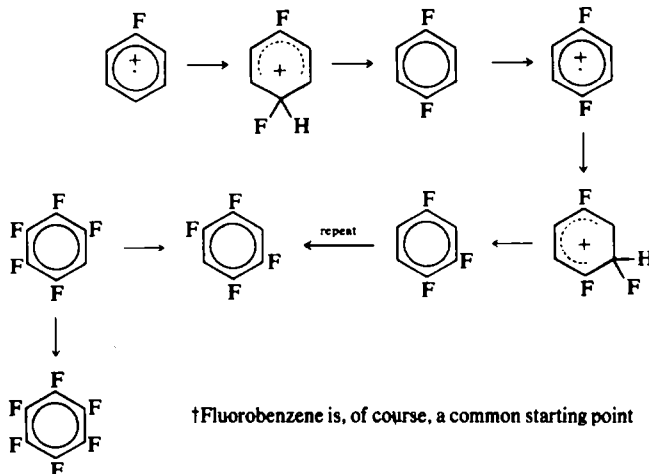
Sequence 3



Sequence 5



Sequence 7 (example sequence shown)



†Fluorobenzene is, of course, a common starting point

ortho and *para* positions. The argument also depends upon their failure to isolate any perfluorocyclohexa-1,3-diene from their low temperature fluorination of hexafluorobenzene.

Unhappily, this conclusion is open to severe criticism upon at least three major grounds. Firstly, these authors have totally failed to consider any reaction sequence analogous to sequence 3 in Table 1, despite the very ionic and oxidising environment, which the surface of the fluorinating agent must present, making sequence 3 *a priori* probably the most acceptable one. Secondly, it is at least possible that any 1,3-diene formed in the fluorination will react further, to yield perfluorocyclohexene, the major product, faster than will the 1,4-diene: the probable ionisation potentials¹⁹ of these compounds make this at least tenable in the absence of experimental contradiction. Thirdly, and most seriously, in our hands the calculations give results substantially at variance with those of Chambers *et al.* (Scheme 3). In our calculations the *para* position is heavily favoured for attack by F⁻ upon the cationic intermediate, whereas attack by F⁻ upon the radical intermediate discriminates but little, albeit still in favour of the 1,4-diene.†

It may be, of course, that Chambers *et al.*'s selection of sequence 1 is correct for their HVMF, but it must be admitted that substantive proof of this is still lacking. All this, therefore, does little to help with the difficulty in the

hydrocarbon case; that is, the impossibility of choosing between sequences 3 and 5 for the fluorination of benzene over CoF₃, KCoF₄, and LiCoF₄.

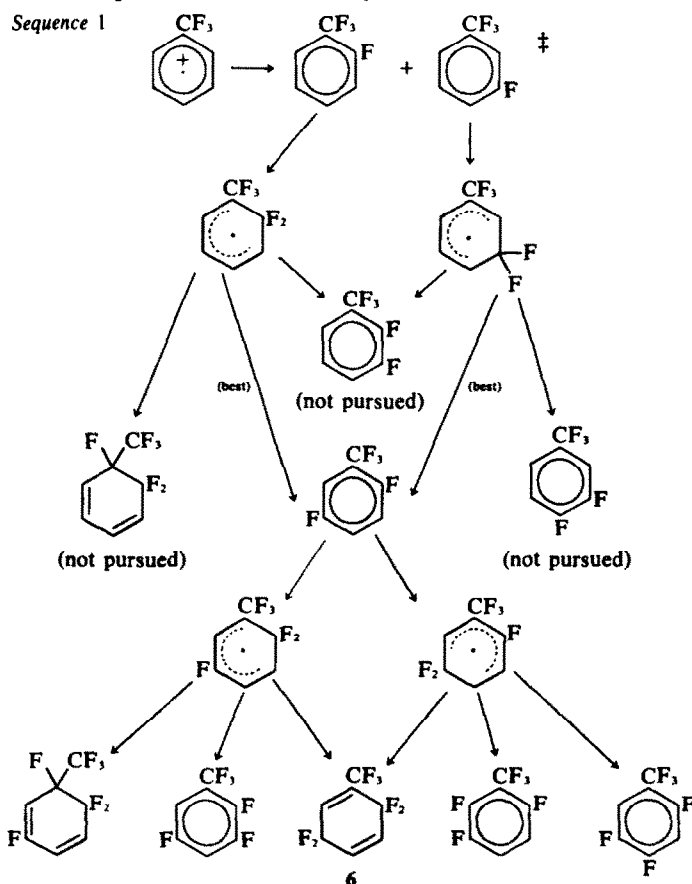
The conclusion from the benzene case must be therefore, that sequences 3 and 5 are both strong contenders for a general mechanism over CoF₃, LiCoF₄, and KCoF₄, but that no *single* sequence explains the CsCoF₄ results—a blend of 3 or 5 with 7 seems to be required here.

Benzotrifluoride. An attempt to distinguish between sequences 3 and 5 may be made by consideration of the known experimental results for benzotrifluoride (BTF) fluorinations. Calculations of the properties of the various compounds and intermediates of interest are set out in Table 3, and these have been used to construct the fluorination routes in diagram 2. Again, nitration data²¹ and Hammett σ^+ values for F and CF₃ have been used, together with calculations (which are not very convincing) for the predictions of sequence 7.

The experimental results for BTF are as follows: over CoF₃,²² fluorination of this substrate gives a complicated mixture of products containing all three pairs of positional isomers of decafluorotrifluoromethylcyclohexane. This result shows that exclusive *p*-fluorination (to give *p*-fluoro-BTF) cannot be the initial step, and that sequence 7, which would leave no 3-H compounds, and possibly even no 2-H, in the mixture, cannot be the sole route either. Studies of the structures of the dihydro- and trihydro-compounds in this product mixture were not conclusive, owing to experimental difficulties in separat-

†Dr. D. T. Clark²⁰ now concurs generally with our spin and charge densities in these intermediates.

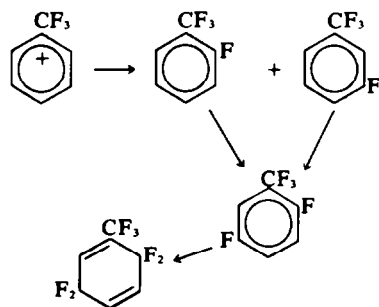
Diagram 2. Predicted fluorination pathways for benzotrifluoride.



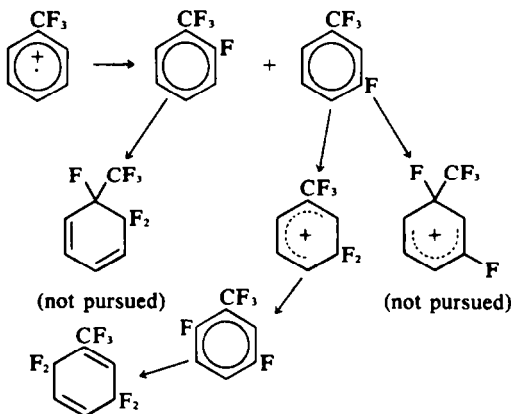
‡If sequence 2 is followed, *ortho*-fluoro BTF if preferred.

Diagram 2 (Contd)

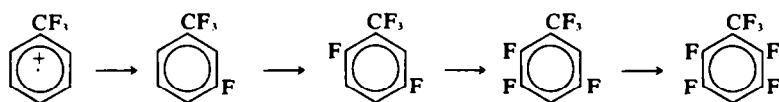
Sequence 3



Sequence 5



Sequence 7



ing the compounds; but they suggest that the initial sequence probably involves 2,5-difluorobenzotrifluoride, or at least removal of the relevant hydrogens.

Over KCoF_4 ,²³ a very large percentage of the product (~50%) is composed of 3,3,6,6-tetrafluoro-1-trifluoromethylcyclohexa-1,4-diene (6) and the compounds derived from this by *cis* and *trans* fluorination of the $\text{CH}=\text{CH}$ bond. The remaining products suggest a more complicated set of origins, but none of them is present in substantial amount. Fluorination of BTF over CsCoF_4 ,²⁴ gives the same diene (6) and some saturation products, together with some polyfluoroaromatics, including 2-fluorobenzotrifluoride, perfluorotoluene and some perfluoromethylcyclohexane. Fluorination over LiCoF_4 ,²⁵ also gives very largely 6 and its *trans* saturation product 2H, 4H/5H - hexafluoro - 1 - trifluoromethyl - cyclohex - 1 - ene.

In this case the results from the CoF_3 fluorinations are not sufficiently detailed to differentiate between sequences 1, 3 and 5, and so need not be considered further from this point of view. They do rule out sequence 7 though; the presence of 2,3,5-trifluorobenzotrifluoride along the major route would mean that no product with a 1-CF₃-3-H arrangement could form, and such compounds

are major products. The results from LiCoF_4 and KCoF_4 reactions are much in favour of scheme 3 as the predominant route, since neither of the others can convincingly explain a (fairly) simple product mixture. The results from CsCoF_4 are not wholly explicable by any of the schemes discussed here.

A related fluorination which may be of interest here is that of perfluorotoluene over CoF_3 at a low temperature.²⁶ This reaction gives a reasonably high concentration of the 1,4-diene heptafluoro - 1 - trifluoromethylcyclohexa - 1,4 - diene (9) in the product mixture, together with a small amount of one of the possible 1,3 dienes (8). As with Chambers *et al.*, however, the bulk of the product (82%) was the monoene, (nonafluoro - 1 - trifluoromethylcyclohexene in this case), which could plausibly have come from the 1,3-diene. Calculations in Table 3 can be used to construct the fluorination pathways shown in diagram 2a.

These pathways show that only sequence 1 predicts both 1,4- and 1,3-diene formation, and that both of the other two suggest exclusive formation of 1,4-diene. Sequence 1 would therefore seem to be the most probable in this case, contrasting strongly with the results from LiCoF_4 ,²⁵ and KCoF_4 ,²³ fluorinations of BTF, which we suggest should correspond to the early stages of the CoF_3

Diagram 2a. Fluorination of perfluorotoluene.

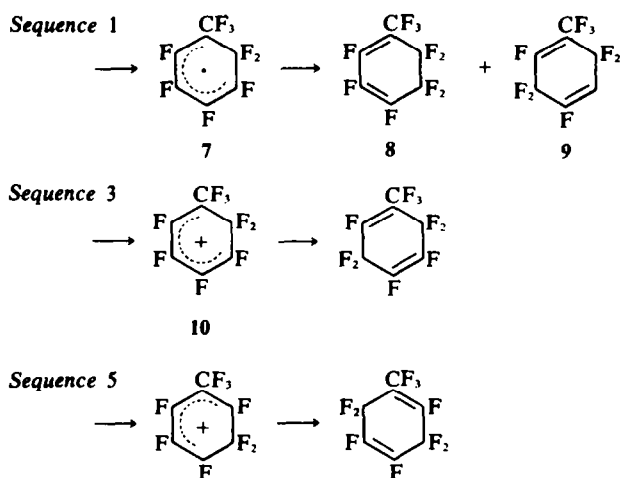








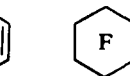


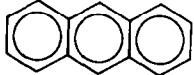
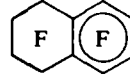
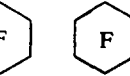
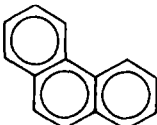
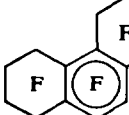
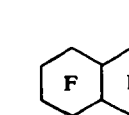


Table 7. Fluorination products from naphthalene, anthracene and phenanthrene

Substrate	Reagent	Products
	CoF ₃	 trace  major  minor
		 major  trace plus di- and poly-hydrocompounds
	KCoF ₄	 major  trace  major
	CsCoF ₄	 11 
	CoF ₃	some hydrogen retained (Ref. 36)
	KCoF ₄ } CsCoF ₄ }	 15  (all in roughly equal amounts)
	CoF ₃	some hydrogen retained (Ref. 36)
	KCoF ₄ , CsCoF ₄	 

fluorination. This difficulty cannot be easily overcome, but we tentatively suggest that sequence 1 prevails here because the high degree of fluorine substitution in radical 7 raises its ionisation potential sufficiently to tip the balance against its oxidation to cation 10 (as sequence 3 demands) and in favour of its quenching by fluorine ligands (as sequence 1 demands). It is also possible that rearrangement is of significance here. It is noteworthy that the favouring of sequence 1 agrees with the conclusions of Chambers *et al.*,⁴ although for the reasons stated earlier we view their arguments with scepticism.

To sum up thus far, scheme 3 appears to be the most generally applicable to the fluorinations of the monocyclic substrates with both the powerful reagent CoF_3 , and the weaker reagents LiCoF_4 and KCoF_4 . The major sequences over CsCoF_4 may also be accommodated on this scheme, but several significant products from this reagent—which gives only simple product mixtures containing few compounds—require sequence 7 or, in the case of BTF, cannot be convincingly explained on any argument thus far advanced.

Naphthalene. This substrate has been recently fluorinated over three reagents currently of interest, viz. CoF_3 ,²⁷ KCoF_4 ,²⁸ and CsCoF_4 .⁷ The bulk of the heavily fluorinated products in each case has been fairly well characterised, and the results are set out in Table 7.

Although the fluorinations were carried out under fairly mild conditions, the vast majority of the hydrogen atoms

are removed in all cases; the KCoF_4 mixture contains very little hydrogen whereas the bulk of the compounds in the CoF_3 product mixture contain at least two hydrogen atoms. The compounds shown for the CoF_3 reaction in Table 7 are those which have been isolated from this complicated mixture, but they comprise only about 30%²⁷ by weight of the product; the remaining 70% probably then consisted of di-, tri and poly-hydro compounds and obvious experimental difficulties have so far precluded their separation and characterisation. These results contrast with the benzene case, where CoF_3 appears to be both the more powerful saturator of double bonds—as is still the case here—and a more powerful hydrogen abstractor. Another interesting point of difference is the presence of appreciable amounts of α -H decalins in the CoF_3 mixture, contrasting with the KCoF_4 result where no α -H compounds at all are present in detectable amounts.

Fluorination of naphthalene with CsCoF_4 ,⁷ gives two major products only; viz. perfluorotetralin and the monene (11). This result is particularly interesting, since no hydrogen-containing material whatever was found amongst the reaction products: we would submit that this result is very strong evidence that the major fluorination pathway in this case goes via perfluoronaphthalene, or some very closely related species.

The various calculations for this substrate under the control of sequences 1, 3 and 5 are set out in Table 5. We have not carried out the calculations for sequence 7

Diagram 3. Predicted fluorination pathways for naphthalene.

Sequence 1

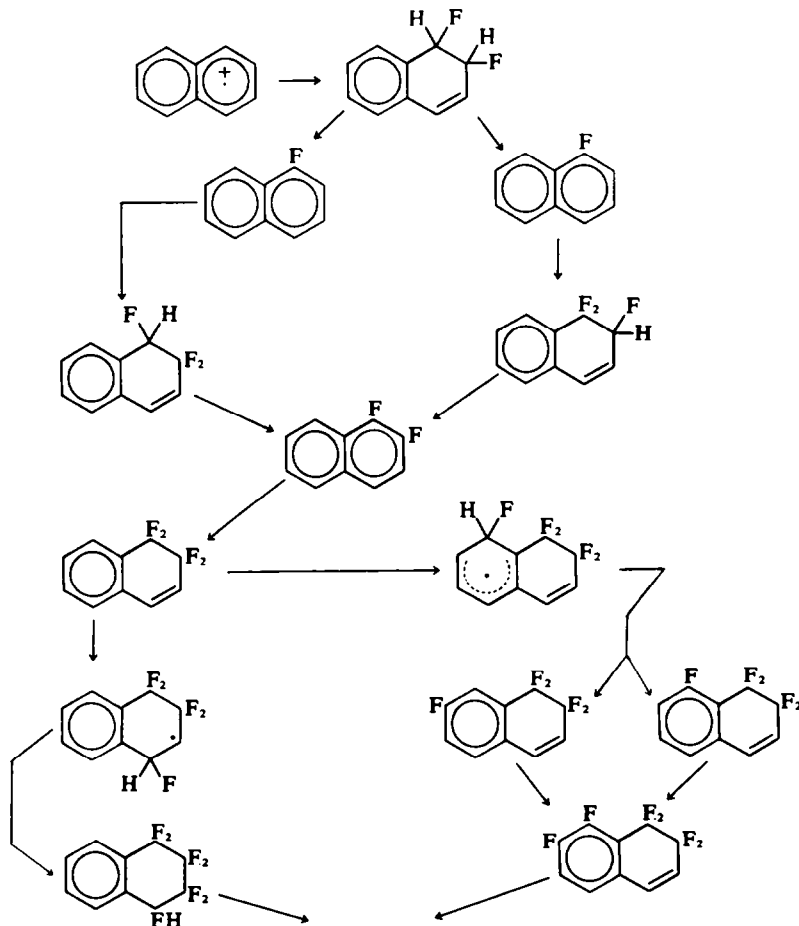
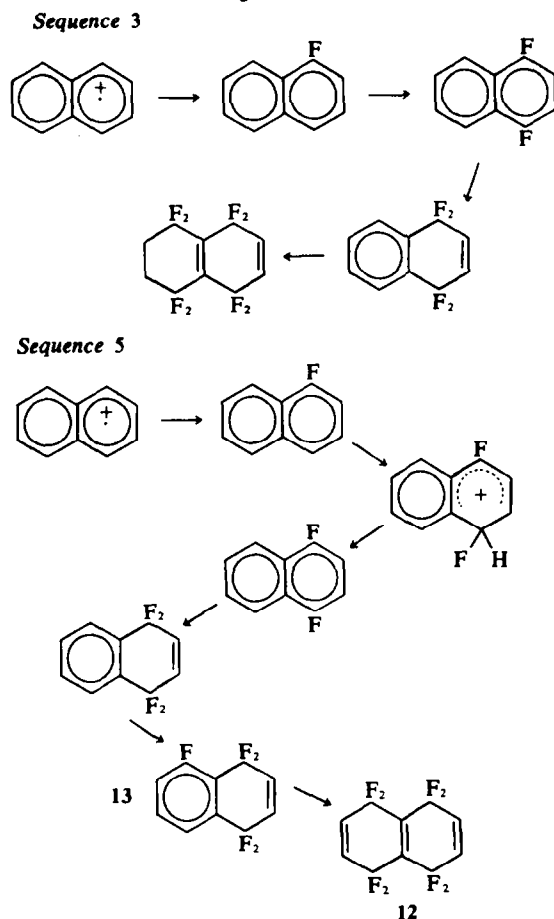


Diagram 3 (Contd)



because the number required would be so large. It would be expected, based on the general patterns of electrophilic substitution in naphthalenes, that the four α -hydrogens would be substituted first, but whether *ipso*-attack or β -substitution would then follow is not obvious.

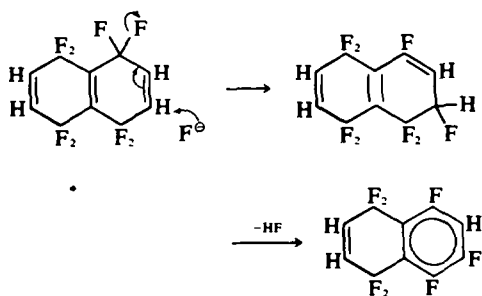
The calculations for sequences 1, 3 and 5 have been used to construct the fluorination pathways set out in diagram 3. Once again, as with the BTF pathways, these diagrams are greatly simplified: a difficulty here—as with BTF results, particularly in sequence 5—is that sometimes several of the calculated spin and/or charge densities are rather similar. This has then led to complexity in the predictions.

These calculated pathways are now to be set against the experimental results. Sequence 1 appears to be a possible runner for the reaction over CoF_3 if hydrogen abstraction (sequence 2) is forbidden, but even here, if sequence 2 is allowed, the β -fluoronaphthalene would be largely suppressed and the pathway would go via the otherwise dominant 1,4 route. If sequence 2 is forbidden, it is not at all clear what should happen after the stages depicted, but it would be at least possible that the experimental product distribution from CoF_3 could materialise.

In contrast, it is very difficult to see how any of the sequences can accommodate the KCoF_4 results; in particular, both sequences 3 and 5 (and possibly 2, as discussed above) lead exclusively through either 12 or compounds very like it. On present ideas, it is very difficult to see how this material might be converted to the highly fluorinated products actually observed. It might be argued that saturation of the hydrogen bearing olefinic

bonds with fluorine, followed by hydrogen abstraction, would at least yield the perfluoromonoene and the β -hydrogen compounds, but if, as has been pointed out, KCoF_4 will not do this reaction for the equivalent benzenoid case with 1, then it is difficult to see why 12 should behave differently.

There is another possibility, which is that a fluoride ion catalysed rearrangement may proceed at this late stage, leading back eventually to aromatic compounds and hence to the observed products:



This rearrangement seems to us to be improbable, since 1 does not rearrange to give 2 over CsCoF_4 (or KCoF_4), and if the reaction to give, eventually, a simple benzene cannot proceed, then there is no reason to suppose that one presently contemplated would proceed either. Such an initial rearrangement would be expected to be thermodynamically disfavoured,²⁹ and no examples of such a rearrangement, from a $-\text{CH}=\text{CH}-$ double bond to a

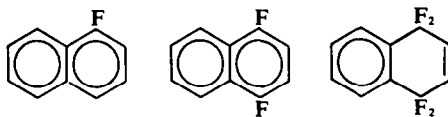
-CH=CF- one, are known. Indeed, thermal defluorination is frequently^{23,30-32} observed rather than such a rearrangement. This superficially attractive possible explanation of the naphthalene fluorination results cannot, therefore, be entertained.

Sequence 7 also is unlikely to explain the CoF₃ results, since it probably does not allow any α -hydrogen to be left (as is required for CoF₃): it may be a possible runner for the KCoF₄ and CsCoF₄ reactions, however.

Indeed, it is very striking that the whole weight of these calculations goes to show how difficult it is to think, within the limits set for this paper, of a fluorination sequence which will leave some hydrogen and, more importantly, a very high degree of fluorination. The results from the CsCoF₄ fluorination⁷ are difficult to explain on sequences 1-6, but sequence 7 may possibly be a runner in this case.

There is, of course, an alternative explanation for the failure of our calculations accurately to predict the fluorination pathways for naphthalene: the calculations may be false or all of our ideas may be wrong. There is, however, good evidence that these calculations do accurately represent the chemistry in other cases; a particularly commanding example in the present case is the electrochemical partial fluorination of naphthalene³³ reported by Rozhkov *et al.* This process depends upon anodic oxidation of the organic substrate and must, in all reason, be a process like Scheme 3 in Table 1 (a multiple ECE process in electrochemical jargon) as these authors

themselves say. The products from this reaction were 1-fluoronaphthalene, 1,4-difluoronaphthalene and 1,1,4,4-tetrafluoro-1,4-dihydronaphthalene (see below); these are precisely the products predicted by our calculations (diagram 3).

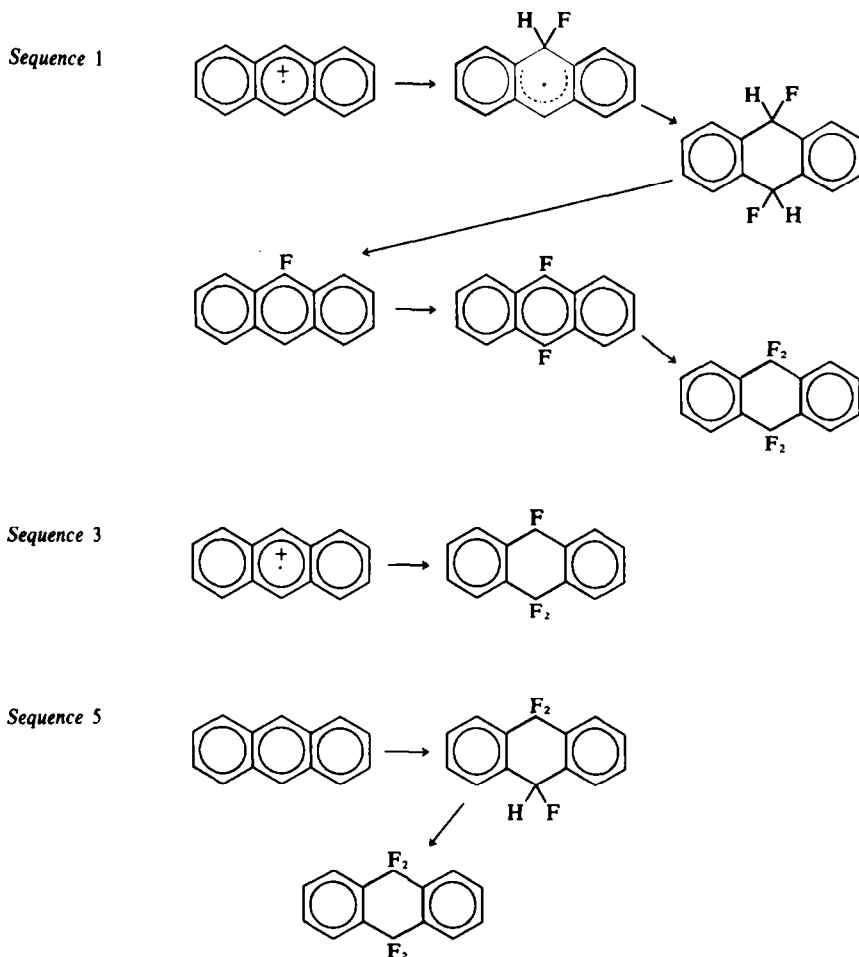


Products from electrochemical fluorination of naphthalene³³

Further support comes from electrochemical acetoxylation and cyanation of naphthalene.³⁴ Again, these processes must approximate closely to sequence 3, that is, formation of a cation radical, quenching by, for example, CN⁻, reoxidation of the radical intermediate at the anode and a final quenching with CN⁻ followed possibly by elimination of HCN. These experiments give, on the one hand, only 1-cyanonaphthalene (no 2-cyano compound was isolated), and on the other a 95:5 mixture of the 1- and 2-acetoxynaphthalenes, with the 1-compound predominant. Interestingly, cyanation of some naphthalenes sometimes replaces a methoxy group with a cyano group, indicating that initial *ipso* substitution is sometimes favoured here.

The final piece of support for the calculations lies in the oxidations of naphthalene with various reagents; it is well

Diagram 4. Predicted fluorination pathways for anthracene.



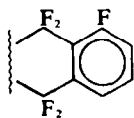
known that these processes proceed via 1-naphthol to naphtho-1,4-quinone with almost all oxidants. Again, these results may be used to support the calculations.

Taken together, these results suggest that the calculations are reliable; and that the difficulty in reconciling the calculations with experiment lies in a genuine weakness of the simple form of cation radical theory—with the cation radical being the product determining intermediate—and not in any calculational inaccuracy. The crux of the difficulty lies, of course, in getting to either perfluoronaphthalene or to a heptafluoronaphthalene; given such a compound as an important intermediate the results could easily be explained.

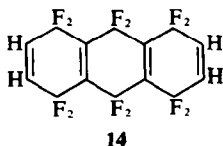
Anthracene. The calculations for anthracene are set out in Table 6; sequence 7 has again not been pursued because of the large number of calculations—each very expensive in computer resources—which would be required. The fluorination pathways predicted (for sequences 1, 3 and 5) are set out in diagram 4.

There is very little agreement here between experiment³⁵—which virtually demands passage through perfluoroanthracene in the fluorination pathways for KCoF_4 and CsCoF_4 —and the calculations which uniformly, and unsurprisingly, predict that 9,9,10,10-tetrafluoro-9,10-dihydroanthracene should be an important intermediate.

If rapid rearrangement were to occur, then this compound might be possible as an intermediate, since it is not a difficult matter to postulate rearrangements which produce, for example, 1,9,10-trifluoroanthracene as final product. Unhappily, even if this expedient is adopted it is to be expected that the 9,9,10,10-tetrafluoro situation will rapidly recur, and with it the same difficulty as with the naphthalene derived intermediate 13; that is, the problem of removing the β hydrogens, since the fragment occurs



both here and in the naphthalene cases, where rapid p -oriented tetrafluorination in the aromatic ring was again predicted. There is no reason to suppose this fragment will behave differently in an anthracene skeleton, and so the routes for sequences 3 and 5 must be expected to go via 14, which will again prove difficult to fluorinate to perfluoro products.

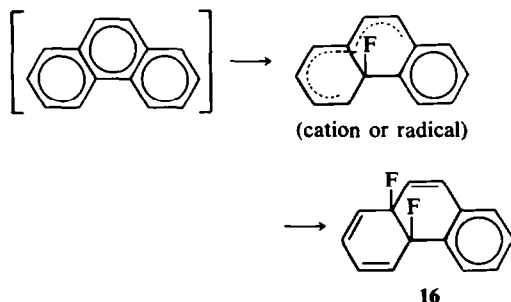


This fluorination pathway, again, can possibly accommodate the CoF_3 fluorination³⁶ results, where extensive fluorination occurs but some hydrogen is retained, even at high temperatures, for a single pass over this reagent; however, none of sequences 1, 3 and 5 can explain either the total removal of hydrogen found with KCoF_4 and with CsCoF_4 (Table 3) or the high concentration of the aromatic compound 15 with no addition across the 9,10 positions. As with naphthalene, sequence 7 might conceivably predict the correct result, but the common occurrence of addition across the 9,10 positions in anthracene reactions makes this rather doubtful.

Once again, the criticism may be levelled at these results that the calculations may be unreliable: this, however, is again refuted by consideration of electrochemical experiments³⁴ where electrochemical oxidation using a platinum/platinum (IV) oxide electrode system gives anthra-9,10-quinone in 90% yield, and cyanation gives a 9-cyano- and 9,10-dicyano-anthracenes. The calculations are therefore again supported by these experiments, and so the explanation of the discrepancy between experiment and calculated fluorination pathways must once more lie with the simplistic form of the theory now under discussion.

Phenanthrene. Only a few calculations have been undertaken for this substrate, because of the very large amount of computer time which an extensive study would require, based on the preliminary calculations reported here. The calculations which have been performed are set out in Table 6.

The electron distributions in the phenanthrene cation radical lead to rather complicated predictions. The initial step would appear to be attack at the 4a-position, followed by formation of 4a,10a-difluoro-4a,10a-dihydrophenanthrene (16)



The subsequent fate of 16 is difficult to predict, since our knowledge of appropriate geometries for the calculations is slender, and so we have concentrated on calculations of the properties of some of the possible monofluorinated cation radicals and of some of the species which might derive from them.

The results of the calculations may be summed up briefly by saying that they (unsurprisingly) predict that the charge controlled initial attacks will all proceed at fluorine-bearing positions, and that the consequently formed Wheland intermediates appear usually to possess the greatest spin or charge densities in the same ring.

We thus predict that for phenanthrene, none of the sequences 1,3 or 5 in Table 1 is likely to give the experimental results (Table 3) over KCoF_4 and CsCoF_4 (no hydrogen at all retained and with the central ring apparently retaining its aromatic character very late on in the fluorination). The experimental results for CoF_3 ¹⁷ are rather poorly defined, but it may be that one of these sequences is possible for this case. Sequence 7 may be a runner for the KCoF_4 and CsCoF_4 fluorinations of this substrate, but data are too scanty for useful comment at this stage.

CONCLUSIONS

The conclusions to be drawn from the work and arguments presented in this paper are as follows, set out in what seems to us to be increasing order of importance:

(i) The simple form of cation radical theory adumbrated by us¹ and by Chambers *et al.*⁴ apparently works

well for the reactions of hydrocarbon monocyclic (benzenoid) aromatics with CoF_3 , LiCoF_4 and KCoF_4 ; for this group of reactions sequence 3 seems to be the most generally satisfactory.

(ii) Even for monocyclics, the reactions involving CsCoF_4 seem to require either a mixture of sequence 3 and sequence 7 (which is not available under Chambers' *et al.*'s⁴ arguments) or something entirely different.

(iii) As the annellation of the substrates increases, so the hypothesis of product control via spin/charge densities in the intermediates becomes rapidly untenable. The difficulty is particularly clear and intractable in the case of anthracene.

(iv) Of the sequences considered here, 7 might well be important (given the experimental results) in the polycyclic fluorinations, but available data are too scanty to permit any definite conclusions.

(v) Overall, then, the hypothesis that the sole product determining features in a fluorination are spin and charge densities in the various intermediates (radical cations, radicals and cations) and that these are well modelled by the expectation values for these parameters in the free (gas phase) species *must be abandoned*.

We shall present a possible way of escape from this difficulty in a later publication.

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