Reactions involving Fluoride Ion. Part 14.[1] Anionic σ-Complexes from Polyfluorinated s-Triazines

By **Richard D. Chambers**,* **Paul D. Philpot**, and **Peter L. Russell**, Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE

The reaction between trifluoro-s-triazine and caesium fluoride in tetramethylene sulphone gave a σ-complex which has been isolated and characterized. Analogous reactions with perfluoro-mono- and -di-isopropyl-s-triazines led to σ-complexes which were detected by [19]F n.m.r. but which were not isolated. No evidence was obtained, however, for the formation of a σ-complex from perfluorotri-isopropyl-s-triazine.

AN analogy is now well established between the roles of fluoride ion and the proton in reactions with unsaturated fluorocarbons and hydrocarbons, respectively, e.g. fluor-ide-ion-induced dimerisation and oligomerisation of fluoro-olefins,[2-7] polyfluoroalkylations of aromatic compounds,[8,9] and rearrangements of perfluoroalkylaromatic

[1] Part 13, R. D. Chambers, J. Hutchinson, and P. D. Philpot, J. Fluorine Chem., 1977, **9**, 15.

[2] W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U.S.P. 2,918,501/1959 (Chem. Abs., 1960, **54**, 20,875).

[3] H. C. Fielding and A. J. Rudge, B.P. 1,082,127 (1967).

[4] D. P. Graham, J. Org. Chem., 1966, **31**, 955.

[5] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, J. Chem. Soc. (C), 1968, 2221.

[6] W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, Chem. Comm., 1970, 1444.

[7] R. D. Chambers, M. Y. Gribble, and E. Marper, J.C.S. Perkin I, 1973, 1710.

[8] S. L. Bell, R. D. Chambers, M. Y. Gribble, and J. R. Maslakiewicz, J.C.S. Perkin I, 1973, 1716, and references therein.

[9] C. T. Drayton, W. T. Flowers, R. N. Haszeldine, and W. D. Morton, J.C.S. Perkin I, 1975, 1035 and references therein.
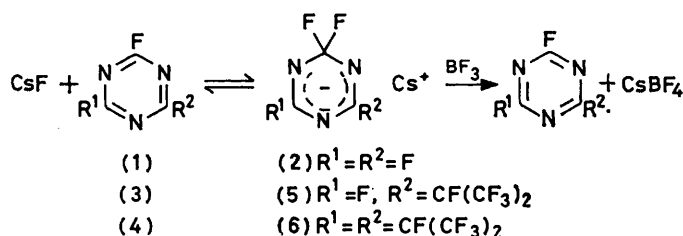
compounds have been observed. Here we extend the analogy by presenting evidence for the formation of σ-complexes in reactions of fluoride ion with an aromatic system.

We have observed that caesium fluoride dissolves quite readily in a solution of trifluoro-s-triazine (1) in tetramethylene sulphone, although its solubility in the sulphone alone is slight, to give a 1 : 1 complex (2). This complex can even be isolated by addition of the solution to stirred toluene, followed by cooling. The ^{19}F n.m.r. spectrum of a solution of (2) in tetramethylene sulphone at 27 °C (Figure) showed only two peaks, at 4 and 51 p.p.m., of equal intensity, in agreement with the proposed structure but progressive addition of boron tri-fluoride–diethyl ether led to regeneration of a sharp peak at 33 p.p.m. due to (1) and disappearance of the peaks at 4 and 51 p.p.m. Furthermore, evaporation of the solution of (2) *in vacuo* provided trifluoro-s-triazine (>80%) and caesium fluoride. Recovery of (1) argues against any other structure for the complex (2); for example, a ring-opened structure might be expected to undergo further reaction. In a variable-temperature study of the ^{19}F n.m.r. spectrum of a solution of (2) in tetramethylene

Again, no ring opening occurred, nor was any significant amount of by-product formed (treatment with boron trifluoride–ether regenerated the starting heterocycle). The ^{19}F n.m.r. spectra of the complexes (5) and (6) at
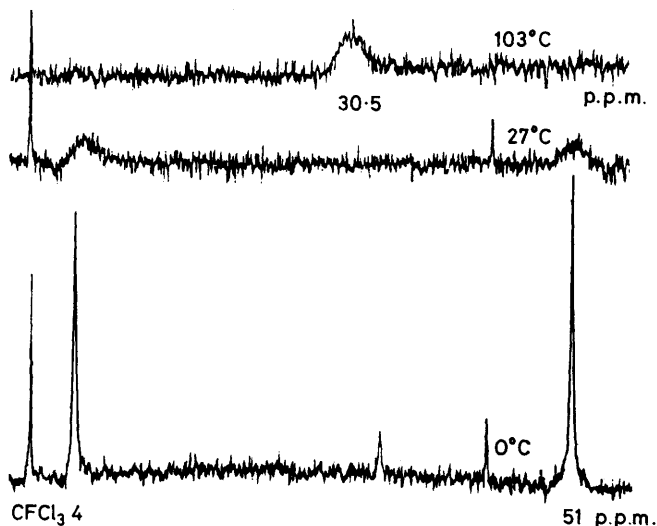
^{19}F N.m.r. spectra of trifluoro-s-triazine–caesium fluoride complex (2) at various temperatures in tetramethylene sulphone

room temperature were only marginally less sharp than the spectrum of (2) at 0 °C (Figure). Thus, introduction of perfluoroisopropyl groups leads to a striking change in equilibrium constant for complex formation, but this change could be due to more than one factor, including relative solubility of the heterocycles (3) and (4), in comparison with (1), in tetramethylene sulphone.

Contrary to our expectations, use of caesium fluoride led to a more favourable equilibrium constant for formation of (2) than use of a 1 : 1 complex of potassium fluoride and the polyether 18-crown-6.[10,11] In the absence of 18-crown-6, there was no evidence for potassium fluoride dissolving in a solution of trifluoro-s-triazine (1). After successive additions of (1) to a solution

(1)   (2) R^1=R^2=F
(3)   (5) R^1=F, R^2=CF(CF$_3$)$_2$
(4)   (6) R^1=R^2=CF(CF$_3$)$_2$

sulphone (Figure), the complete disappearance of all signals was observed on raising the temperature to 60 °C, but on further heating to 103 °C a single broad band was observed at 30.5 p.p.m. The position of this resonance is intermediate between that of trifluoro-s-triazine (1) and the midpoint (27.5 p.p.m.) of the two signals arising from the complex, which indicates rapid exchange at this temperature amongst (1), the σ-complex (2), and fluoride ion. On cooling to 0 °C, the original spectrum of the complex was again obtained, confirming that no other reaction had taken place. The origin of the two small peaks in the spectra (see Figure) is uncertain, but their integrated intensity is very small in comparison with the other bands.

Reactions between caesium fluoride and perfluoro-mono- (3) and -di- (4) isopropyl-s-triazines occurred, giving complexes (5) and (6); the production of a complex from (4) was particularly dramatic since this triazine is insoluble in tetramethylene sulphone.

The ^{19}F n.m.r. spectrum of the complex (5) was clear-cut (see Table), giving absorptions corresponding to CF$_2$ and ring fluorine in the same regions as those for (2). As anticipated, the complex (6), containing two perfluoroisopropyl groups, showed an absorption corresponding to CF$_2$ but none corresponding to a ring fluorine atom.

of potassium fluoride–18-crown-6 in tetramethylene sulphone the ^{19}F n.m.r. spectra showed a signal corresponding to (1) in every case; however, the signal was extensively broadened except when an excess of (1) had been added. A very broad signal at *ca.* 160 p.p.m. also occurred, probably associated with fluoride ion, but in no case were any signals corresponding to the complex (2) observed, even in the presence of an excess of fluoride ion.

Complexes (2), (5), and (6) are the first anionic σ-complexes derived from completely fluorinated aromatic systems which have been characterised, although a 1 : 1 complex between caesium fluoride and hexafluorocyclo-

^{19}F Chemical shifts (p.p.m. upfield from CFCl$_3$)

Hetero-cycle	Ring F	CF	CF$_3$	σ-Complex	CF$_2$	Ring F	CF	CF$_3$
(1)	33			(2)	4	51		
(3)	32	183	74	(5)	2	50	183	74
(4)	32	184	74	(6)	1		184	74

[10] G. W. Gokel and D. J. Cram, *J. Org. Chem.*, 1974, **39**, 2445.

[11] C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.*, 1974, **96**, 2250.

triphosphazene has been reported.[12] Additions of fluoride ion to 1,3,5-trinitrobenzene [13] in benzene and to picryl fluoride [14] in acetonitrile, by using potassium fluoride–crown complexes have been observed, giving the complexes (7) and (8) repectively but the equilibrium concentration of (7) was insufficient for detection by n.m.r.[14] The signal associated with CF_2 in (8) showed a large (54 p.p.m.) downfield shift from the value for fluorine in picryl fluoride, which is consistent with the direction of shift for CF_2 in the complexes (2), (5), and (6). In the light of our results, it is probable that use of caesium fluoride in tetramethylene sulphone would lead to a greater equilibrium concentration of the complex (7); indeed, there may have been a tendency to over-emphasize the value of crown polyethers in generating reactive fluoride systems.

Most σ-complexes that have been described [15,16] so far contain nitro-groups; a good deal of the charge probably resides on these groups,[17] but there are some examples where the charge is more clearly associated with the aromatic ring itself, for example, the reactions of amide ion in liquid ammonia with s-triazines,[18] quinoline, isoquinoline,[19] and other nitrogen heterocyclic systems.[20,21] Complexes (2), (5), and (6) clearly fall into this category.
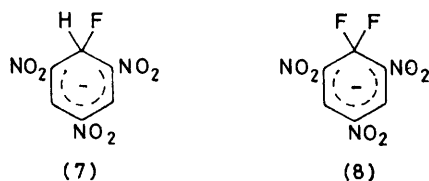
The chemical behaviour of the complex (2) is also of interest: conceivably, it could act as either a nucleophile or a source of fluoride ion. So far, however, all attempts at nucleophilic displacement, e.g. with acetyl chloride at room temperature or t-butyl chloride at 100 °C, have resulted in fluoride ion donation and regeneration of trifluoro-s-triazine.

When equimolar quantities of trifluoro-s-triazine (1) and caesium fluoride were heated in the absence of a solvent to 180 °C in a sealed, evacuated Carius tube a pale yellow glass was obtained. This is only sparingly soluble in tetramethylene sulphone and the [19]F n.m.r. spectrum does not correspond to that of the complex (2). The identity of this product has not been established; however it probably arises from a ring opening process, because (1) cannot be recovered from it by adding boron trifluoride–ether.

Under conditions similar to those described above for reactions with the triazines (1), (3), and (4), no complex

between perfluorotri-isopropyl-s-triazine and caesium fluoride in tetramethylene sulphone was detected.

EXPERIMENTAL

[19]F N.m.r. spectra were recorded with a Brüker HX90 E instrument at 84.675 MHz with deuterium lock at 13.811 MHz [D_2O or $(CD_3)_2CO$ capillary] and $CFCl_3$ as internal standard; upfield shifts are quoted as positive. Computer-averaged spectra were accumulated with a Brüker B-NC 12 data system. Tetramethylene sulphone was redistilled *in vacuo* and stored over molecular sieves. Trifluoro-s-triazine was transferred *in vacuo* immediately before use. Perfluoroisopropyl-s-triazines were obtained by published methods.[22,23] All reactions and manipulations were carried out, as far as possible, under dry nitrogen in apparatus that had been baked in an oven and purged with dry nitrogen. Caesium fluoride (B.D.H. reagent grade) was dried by heating (160 °C) under high vacuum for 24 h, ground to a fine powder in a glove bag, and then heated under vacuum for a further 24 h.

Formation of σ-Complexes.—(a) *From* trifluoro-s-triazine (1). Trifluoro-s-triazine (1) (7.95 g, 58.9 mmol) was transferred *in vacuo* into a small flask containing tetramethylene sulphone (35 ml), and caesium fluoride (8.9 g, 58.5 mmol) was added. The mixture was stirred for 24 h; the [19]F n.m.r. spectrum of the supernatant liquid showed δ *ca.* 4br, 33br and 51br p.p.m. Some undissolved material (see later) was filtered off and the clear pale yellow filtrate was added to toluene (100 ml) and cooled rapidly to yield a white gelatinous precipitate of the complex (2). This was then filtered free of as much solvent as possible under slight vacuum and redissolved in the sulphone (40 ml), giving [19]F δ *ca.* 4br and *ca.* 51br p.p.m. (see Figure). Progressive addition of boron trifluoride–diethyl ether to the solution gave a white precipitate of caesium tetrafluoroborate with eventual regeneration of (1), [19]F δ 33 p.p.m. Undissolved solid removed by the initial filtration was shown to be the complex (2), since it dissolved in tetramethylene sulphone and afforded the triazine (1) on addition of boron trifluoride–diethyl ether. A sample of the solid complex (2) was heated *in vacuo* while connected to a cold trap, and volatile products were collected at various temperatures. G.l.c. analysis showed the presence of trifluoro-s-triazine (1) and toluene. [19]F N.m.r. spectra of a solution of (2) in tetramethylene sulphone were recorded at various temperatures (see Figure). Acetonitrile was added to prevent solidification before reducing the temperature to −40 °C; the spectrum at this temperature was identical with that recorded at 0 °C

(b) *From perfluoroisopropyl-s-triazine* (3). A mixture of perfluoroisopropyl-s-triazine (0.29 g, *ca.* 1 mmol) and caesium fluoride (0.15 g, 1 mmol) in tetramethylene sulphone (1 ml) was stirred vigorously for 46 h; a sample of the solution gave [19]F n.m.r. signals due to the complex (5); δ 1.8 (CF_2), 49.5 (CF), 73.7 ($CF_3 \cdot CF$), and 183.3 p.p.m. ($CF_3 \cdot CF$). Progressive addition of boron trifluoride–diethyl ether led to

[12] W. M. Douglas, M. Cooke, M. Lustig, and J. K. Ruff, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 409.

[13] A. R. Butler, *J.C.S. Perkin I*, 1975, 1557.

[14] F. Terrier, G. Ah-Kow, M. J. Pouet, and M. P. Simonnin, *Tetrahedron Letters*, 1976, 227.

[15] M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211.

[16] M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

[17] P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 848.

[18] G. Simig, H. C. van der Plas, and C. A. Landheer, *Rec. Trav. chim.*, 1976, **95**, 113.

[19] J. A. Zoltewicz, L. S. Helmick, T. M. Oestreich, R. W. King, and P. E. Kandetzki, *J. Org. Chem.*, 1973, **38**, 1947.

[20] J. P. Geerts, C. A. H. Rasmussen, H. C. van der Plas, and A. van Veldhuizen, *Rec. Trav. chim.*, 1974, **93**, 231.

[21] D. E. Klinge and H. C. van der Plas, *Rec. Trav. chim.*, 1975, **94**, 233.

[22] W. R. Deem, B.P. 1,148,676/1969.

[23] R. L. Dressler and J. A. Young, *J. Org. Chem.*, 1967, **32**, 2004.

the gradual disappearance of this spectrum and appearance of signals due to the parent heterocycle (3) [δ 32.2 (ring F), 73.6 ($CF_3 \cdot CF$), 151.7 ($CsBF_4$), and 183.1 p.p.m. ($CF_3 \cdot CF$)].

[19]F N.m.r. spectra of the complex were recorded at a number of temperatures from 25 to 105 °C. There was no change on lowering the temperature, before eventual solidification, but on raising the temperature the low-field resonances (δ 1.8 and 49.5) disappeared in the region 57—87 °C, leaving only the signals due to the perfluoroisopropyl group; only the original spectrum reappeared on lowering the temperature.

Addition of toluene to a solution of the complex (5) followed by cooling gave no precipitate. The [19]F n.m.r. spectrum of the resultant solution showed the two low field resonances (δ 1.8 and 49.5 p.p.m.), but the signals were so broad that they were almost indistinguishable from the base line. This indicates that the addition of toluene increases the rate of fluoride ion exchange.

(c) *From perfluorodi-isopropyl-s-triazine* (4). A mixture of perfluorodi-isopropyl-*s*-triazine (1.14 g, 2.6 mmol) and caesium fluoride (0.45 g, *ca.* 3 mmol) in tetramethylene sulphone (3.5 ml) was stirred vigorously for 75 h; a sample gave [19]F n.m.r. signals due to the complex (6): δ 1.3 (CF_2), 73.9 ($CF_3 \cdot CF$), and 183.8 p.p.m. ($CF_3 \cdot CF$). Progressive addition of boron trifluoride–diethyl ether led to gradual disappearance of this spectrum and appearance of signals due to the parent heterocycle (4) [δ 31.5 (ring F), 73.7 ($CF_3 \cdot CF$), 152 ($CsBF_4$), and 183.6 p.p.m. ($CF_3 \cdot CF$)].