Radiotracers in Fluorine Chemistry. Part 12.[1] Reactions between Caesium Fluoride and Arsenic Pentafluoride, Boron Trifluoride, Sulphur Tetrafluoride, Carbonyl Fluoride, and Carbon Dioxide Under Heterogeneous Conditions at Room Temperature. Radiotracer Studies using Fluorine-18, Sulphur-35, and Carbon-14†

Kim W. Dixon and John M. Winfield*
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Activation of CsF by thermal decomposition of its 1 : 1 adducts with hexafluoroacetone or carbonyl fluoride results in significantly greater activity with respect to its reactions with AsF_5, BF_3, and SF_4 under heterogeneous conditions at room temperature, and enables reactions involving carbonyl fluoride and carbon dioxide to be studied. The results of radiotracer experiments employing ^{18}F and ^{35}S or ^{14}C are consistent with the occurrence of weakly adsorbed SF_4 or F_2CO at the surface of activated CsF in addition to permanently retained species SF_5^- and F_3CO^-. Carbon dioxide interacts weakly with activated CsF. Room-temperature ^{18}F exchange occurs between ^{18}F-labelled F_2CO and activated CsF. It is not observable in the other systems but does occur at 373 K. It is suggested that the CsF activation process results in a pore structure for the solid and that this is responsible for its increased reactivity.

The activation of alkali-metal fluorides by formation of Lewis acid–base complexes and their subsequent decomposition is commonly used to increase reactivity. For example it is desirable to treat sodium or potassium fluoride with anhydrous hydrogen fluoride or uranium hexafluoride followed by thermal decomposition of the adducts formed prior to their use as Lewis bases towards molybdenum, tungsten, or uranium hexafluoride,[2] and caesium and potassium fluorides are activated by the formation and subsequent thermal decomposition of their hexafluoroacetone adducts prior to their use in nitrosyl fluoride synthesis.[3] Similar considerations apply to the use of CsF as a heterogeneous catalyst. We have shown that CsF activated by the $(CF_3)_2CO$ route is superior to thermally activated material as a catalyst for chlorofluorination of sulphur tetrafluoride.[4] One effect of activation is to produce materials of greatly increased surface areas.[5]

Despite its importance, a systematic quantitative comparison between activated and untreated CsF has not been reported previously. This is the subject of the present work in which fluorine-18 (β^+ decay, $t_{\frac{1}{2}} = 110$ min) together with the β^- emitters carbon-14 and sulphur-35 as appropriate have been used to study Lewis acid–base reactions involving CsF under heterogeneous conditions at room temperature. The use of ^{18}F-labelled Lewis acids enables reaction stoicheiometries to be determined, for example the formation of the compound Na_2UF_8 from the heterogeneous reaction between NaF and UF_6 has been demonstrated.[6] The combination of fluorine-18 and carbon-14 or sulphur-35 experiments enables inferences to be drawn about the nature of the surface species formed.

Results and Discussion

Activation of Caesium Fluoride.—The reaction of caesium fluoride with hexafluoroacetone in the presence of acetonitrile leads to caesium heptafluoroisopropoxide.[7] Its thermal decomposition in a Monel metal vessel at 398 K for 16 h *in vacuo* gave an off-white solid that had the appearance of talc. The B.E.T. (Brunauer, Emmett, and Teller) areas using krypton-85 as adsorbate,[5,8] of samples from five different preparations were in the range 3.01—2.09 $m^2\ g^{-1}$ (95% confidence limits) compared with those of untreated CsF which were in the range 0.31—0.19 $m^2\ g^{-1}$. Decomposition of $Cs[OCF(CF_3)_2]$ under the conditions used here was expected to be complete,[7] however the i.r. spectrum and analysis of the solid produced indicated some retention of the $[(CF_3)_2CFO]^-$ anion, the composition being 99.5 CsF, 0.5 $Cs[OCF(CF_3)_2]$.

Thermal decomposition of caesium trifluoromethoxide[9] at 393 K for 3 h *in vacuo* gave CsF of similar appearance to that described above whose B.E.T. area was in the range 2.27—1.77 $m^2\ g^{-1}$. The $[CF_3O]^-$ anion was not detected in this material.

The B.E.T. data are based on a more extensive study than our previous values for CsF.[5] The values are larger than those obtained previously since in the present work, following usual practice,[10] the saturation vapour pressure of supercooled Kr at 77 K was used rather than that of solid Kr. Both studies indicate a ten-fold increase in B.E.T. area however when CsF is activated *via* the $(CF_3)_2CO$ reaction. The increase is too large to be due simply to a reduction in the particle size of CsF. It could be argued that the small quantity of the $[(CF_3)_2CFO]^-$ anion retained after thermal decomposition of $Cs[OCF(CF_3)_2]$ creates disorder in the CsF lattice leading to higher B.E.T. areas, however the B.E.T. area of CsF obtained from decomposition of $Cs[OCF_3]$ is almost as high, and this explanation seems unlikely.

Decomposition reactions in which one solid is converted into a second with evolution of gas are known to result in the development of a pore system with an associated increase in surface area.[10] Good B.E.T. data were obtained and it is considered that the most likely explanation is that CsF produced from decompositions of perfluorinated alkoxides has a meso- or macro-porous structure.[11] If micropores were present, apparent B.E.T. areas would be much higher and satisfactory isotherms would not be expected.[12]

Reactions of Caesium Fluoride with ^{18}F-Labelled Arsenic Pentafluoride or Boron Trifluoride.—Admission of ^{18}F-labelled arsenic pentafluoride or boron trifluoride to solid CsF samples, either untreated, or activated by the $(CF_3)_2CO$ route, at room temperature led to a rapid growth of ^{18}F activity in the solid over the first 10—40 min of reaction and a constant count rate

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† *Non-S.I. unit employed:* Torr ≈ 133 Pa.

Table 1. Reactions between caesium fluoride and ^{18}F-labelled arsenic pentafluoride, boron trifluoride, or sulphur tetrafluoride at room temperature

	^{18}F Specific count rate of the volatile fluoride/count min^{-1} mmol^{-1}			
Pretreatment of CsF	Before reaction	After reaction	^{18}F Count rate of solid/count min^{-1}	Uptake of volatile fluoride/mmol[a]
(*i*) CsF (3.29 ± 0.06 mmol) + $AsF_4{}^{18}F$ (1.0 ± 0.01 mmol)[b]				
$(CF_3)_2CO$–MeCN	13 567 ± 116	13 567 ± 116	11 538 ± 107	0.85 ± 0.01
	7 755 ± 88	7 751 ± 88	6 747 ± 82	0.87 ± 0.01
	10 647 ± 103	10 647 ± 103	8 837 ± 94	0.83 ± 0.01
	4 236 ± 65	4 235 ± 65	3 722 ± 61	0.88 ± 0.01
None	8 932 ± 95	8 930 ± 95	4 377 ± 66	0.49 ± 0.01
	10 647 ± 103	10 647 ± 103	5 324 ± 73	0.50 ± 0.01
	11 398 ± 107	11 398 ± 107	5 910 ± 77	0.52 ± 0.01
	4 236 ± 65	4 235 ± 65	2 033 ± 45	0.48 ± 0.01
(*ii*) CsF (3.29 ± 0.06 mmol) + $BF_2{}^{18}F$ (1.0 ± 0.01 mmol)[b]				
$(CF_3)_2CO$–MeCN	15 003 ± 123	65 ± 8[c]	14 995 ± 120	1.00 ± 0.01
	12 118 ± 110	51 ± 7[c]	12 056 ± 110	1.00 ± 0.01
	6 870 ± 83	43 ± 7[c]	6 869 ± 83	1.00 ± 0.01
	16 781 ± 130	81 ± 9[c]	16 750 ± 130	1.00 ± 0.01
None	14 326 ± 120	14 362 ± 120	1 275 ± 36	0.09 ± 0.01
	9 513 ± 97	9 511 ± 97	894 ± 30	0.09 ± 0.01
	12 118 ± 110	12 115 ± 110	1 030 ± 32	0.085 ± 0.01
	5 316 ± 73	5 313 ± 73	457 ± 21	0.09 ± 0.01
(*iii*) CsF (3.29 ± 0.06 mmol) + $SF_3{}^{18}F$ (1.0 ± 0.01 mmol)[b]				
$(CF_3)_2CO$–MeCN	5 270 ± 73	5 270 ± 73	1 560 ± 40	0.30 ± 0.01
	4 117 ± 64	4 109 ± 64	1 276 ± 36	0.31 ± 0.01
	1 967 ± 44	1 961 ± 44	560 ± 24	0.29 ± 0.01
	2 516 ± 50	2 514 ± 50	729 ± 27	0.29 ± 0.01
None	4 217 ± 65	4 215 ± 65	181 ± 13	0.04 ± 0.01
	3 557 ± 60	3 558 ± 60	142 ± 12	0.04 ± 0.01
	2 516 ± 50	2 509 ± 50	97 ± 10	0.04 ± 0.01
	2 733 ± 52	2 731 ± 52	127 ± 11	0.05 ± 0.01

[a] Determined from the count rate of the solid and the specific count rate of the volatile fluoride. [b] Initial pressure 300 ± 2 Torr. [c] Count rate (count min^{-1}) of total BF_3 in the gas phase after reaction.

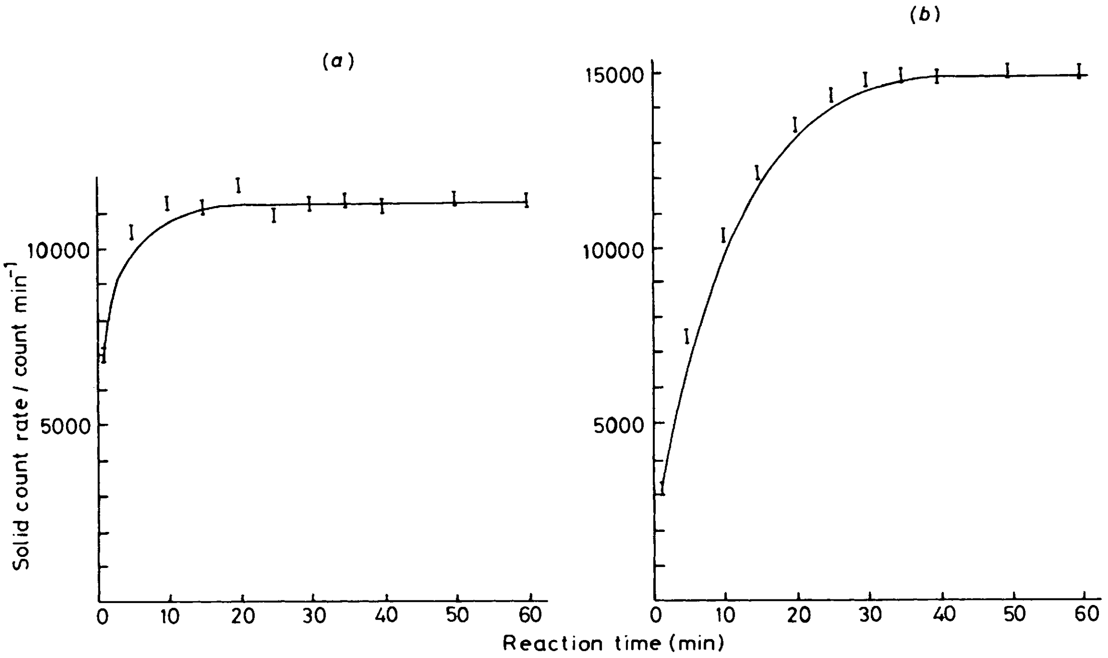

Figure 1. Solid fluorine-18 count rate *vs.* time for (*a*) $AsF_4{}^{18}F$ (1.0 mmol) + activated CsF (3.29 mmol) and (*b*) $BF_2{}^{18}F$ (1.0 mmol) + activated CsF (3.29 mmol)

Table 2. Fluorine-18 exchange between ^{18}F-labelled boron trifluoride and lithium or caesium tetrafluoroborate in the presence of acetonitrile after 1 h at room temperature

	^{18}F Count rate of $BF_2{}^{18}F$/count min^{-1}				
BF_3/mmol	Initial	After 1 h	ABF_4/mmol	^{18}F Count rate of ABF_4/count min^{-1}	Fraction ^{18}F exchanged[a]
2.70	15 966 ± 126	6 856 ± 83	2.65[b]	9 003 ± 95	1.02
2.00	17 261 ± 131	14 215 ± 119	1.95[c]	2 926 ± 54	0.30

[a] Defined by $A_1(A_1 + A_2)^{-1}/[4m_1(4m_1 + 3m_2)^{-1}]$ where A_1 and A_2/count min^{-1} are ^{18}F count rates of m_1 mmol ABF_4 and m_2 mmol BF_3 after reaction. [b] $LiBF_4$. [c] $CsBF_4$.

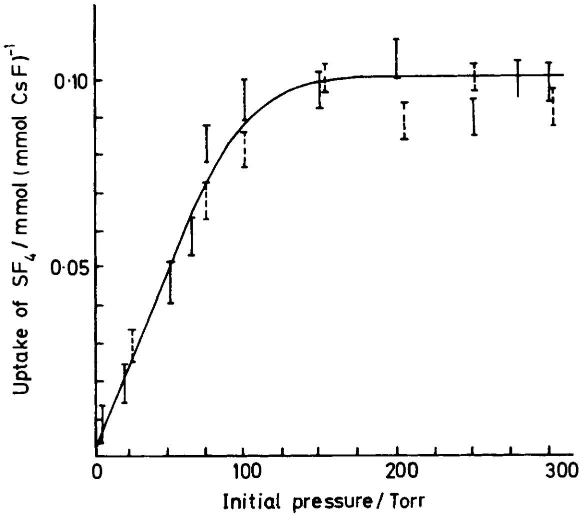

Figure 2. Relationship between uptake of SF_4 by activated CsF and the initial pressure of SF_4; I, manometric measurement; ⁝, ^{18}F measurement

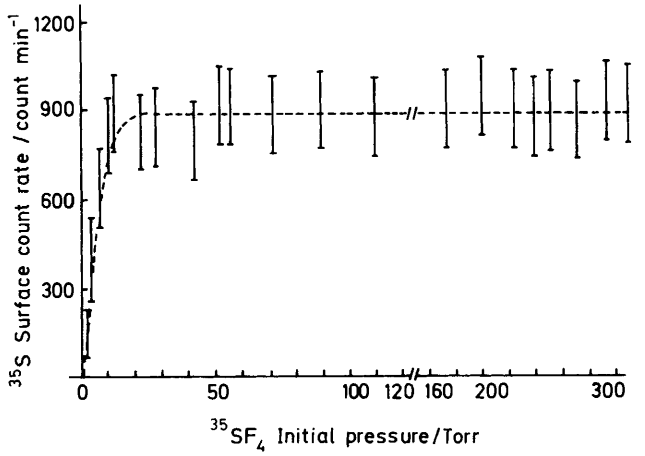

Figure 3. Variation of sulphur-35 surface count rate at activated CsF with the initial pressure of SF_4

from the solid thereafter. The behaviour observed is illustrated by $AsF_4{}^{18}F$ and $BF_2{}^{18}F$ *versus* activated CsF, Figure 1. There was no observable ^{18}F exchange between $AsF_4{}^{18}F$ and CsF although exchange did occur at 398 K, hence ^{18}F count rates of the solids after removal of $AsF_4{}^{18}F$ are a direct measure of the uptake of AsF_5 by CsF, Table 1. The uptake of ^{18}F is irreversible at room temperature as neither prolonged pumping nor admission of inactive AsF_5 had any effect on the count rates.

The reactions between activated CsF and $AsF_4{}^{18}F$ were very exothermic and the average uptake of AsF_5 determined was 0.26 ± 0.02 mmol (mmol CsF)$^{-1}$. Treatment of activated CsF with an equal quantity of inactive AsF_5 prior to admission of $AsF_5{}^{18}F$ resulted in similar behaviour to that shown in Figure 1(*a*) but a smaller uptake of AsF_5, 0.24 ± 0.02 mmol (mmol CsF)$^{-1}$. The uptakes of AsF_5 by untreated CsF were even smaller, Table 1, the average value being 0.15 ± 0.02 mmol (mmol CsF)$^{-1}$, and the admission of AsF_5 prior to $AsF_4{}^{18}F$ resulted in no observable interaction. In all cases the AsF_6^- anion was detected by i.r. spectroscopy in the solids after reaction but there was no evidence for the $[(CF_3)_2CFO]^-$ anion nor for $[As_2F_{11}]^-$.

The behaviour of $BF_2{}^{18}F$ towards untreated CsF, Table 1, was analogous to that of $AsF_4{}^{18}F$ but uptakes were very small; the average value was 0.03 ± 0.01 mmol (mmol CsF)$^{-1}$. Using identical reaction conditions complete reaction was observed, however, if CsF was activated by $(CF_3)_2CO$ or F_2CO treatments, Table 1. These reaction stoicheiometries were therefore determined manometrically and the BF_3 uptakes were 0.99 ± 0.1 and 0.95 ± 0.1 mmol (mmol CsF)$^{-1}$ respectively for CsF activated *via* $(CF_3)_2CO$ and *via* F_2CO. The uptake by CsF that had been calcined at 423 K *in vacuo* was 0.33 ± 0.1 mmol (mmol CsF)$^{-1}$ and this material is significantly less reactive than CsF activated by chemical means.

In all cases the only species detected by i.r. spectroscopy after reaction was the BF_4^- anion. There was no detectable ^{18}F exchange between $BF_2{}^{18}F$ and $CsBF_4$ or between ^{18}F-labelled $CsBF_4$ and BF_3 under heterogeneous conditions at room temperature. Exchange was observed at 373 K and also at room temperature, Table 2, in the presence of acetonitrile a solvent in which $CsBF_4$ is soluble to some extent. Complete ^{18}F exchange was observed between $BF_2{}^{18}F$ and $LiBF_4$ under homogeneous conditions in MeCN and this is consistent with a previous ^{19}F n.m.r. observation of rapid exchange of fluorine among boron atoms in a MeCN solution of $AgBF_4$.[13]

Reactions of Caesium Fluoride with ^{18}*F- or* ^{35}*S-Labelled Sulphur Tetrafluoride.*—A brief account of some of these results has been given in a preliminary communication.[14] The increases in ^{18}F activity with time observed in the solid when ^{18}F-labelled sulphur tetrafluoride was admitted to either untreated CsF or to CsF activated *via* $(CF_3)_2CO$ were similar in form to that in Figure 1(*b*). There was no observable ^{18}F exchange in either case and the uptakes of SF_4 determined from such experiments are given in Table 1. The average SF_4 uptake for activated CsF was 0.09 ± 0.01 mmol (mmol CsF)$^{-1}$ and that for untreated CsF was 0.01 ± 0.005 mmol (mmol CsF)$^{-1}$, a similar ratio to that of the surface areas of the solids. A series of experiments using initial pressures of $SF_3{}^{18}F$ in the range 50—300 Torr and experiments in which SF_4 uptakes were determined manometrically indicated that uptake by activated CsF was independent of the initial pressure in the range 100—300 Torr, Figure 2. The SF_5^- anion was detected by i.r. spectroscopy after these reactions but there was no evidence for $[(CF_3)_2CFO]^-$.

Table 3. Reaction between activated caesium fluoride (3.29 ± 0.06 mmol) and ^{18}F-labelled carbonyl fluoride (0.94 ± 0.01 mmol) at room temperature[a]

^{18}F Specific count rate of F_2CO/count min^{-1} mmol^{-1}		Fraction of ^{18}F activity exchanged	Estimated[b] uptake of F_2CO/mmol
Before reaction	After 120 min		
7 139 ± 85	5 927 ± 76	0.27	0.19
7 139 ± 85	5 919 ± 76	0.27	0.20
5 130 ± 71	4 370 ± 66	0.27	0.20

[a] Reaction time 120 min, CsF activated by $(CF_3)_2CO$–MeCN treatment, initial pressure 300 ± 2 Torr. [b] After making allowance for ^{18}F activity in CsF due to exchange.

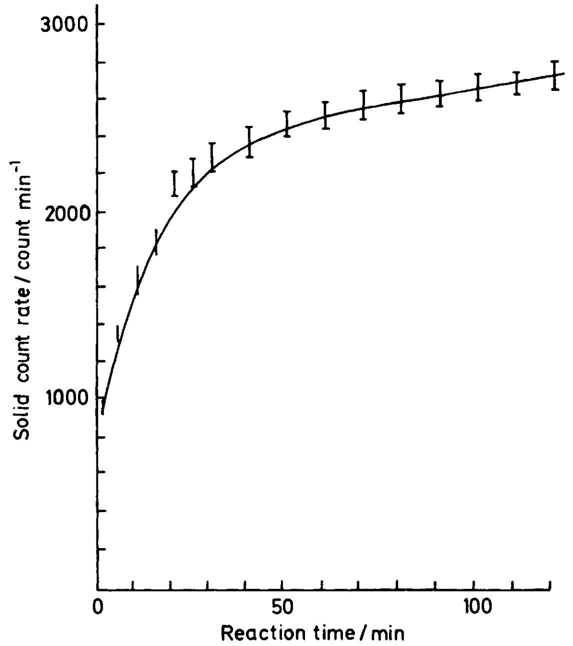

Figure 4. Solid fluorine-18 count rate *vs.* time for ^{18}FFCO (0.94 mmol) + activated CsF (3.29 mmol)

The interaction of [^{35}S]sulphur tetrafluoride with activated CsF was studied at 21 initial pressures between 2 and 308 Torr. The ^{35}S count from the surface increased rapidly during the first 10 min thereafter remaining constant and saturation coverage was achieved at pressures above 10 Torr, Figure 3. Removal of gaseous $^{35}SF_4$ led to the loss of 85% of the ^{35}S surface activity. This could be restored to 90% of its original value by adding a further $^{35}SF_4$ aliquot. The overall uptake of SF_4 by surface and bulk CsF as determined from the decrease in the gas-phase $^{35}SF_4$ count was 0.10 ± 0.02 mmol (mmol CsF)$^{-1}$ which is in good agreement with the uptake determined from the ^{18}F experiments.

Reactions of Activated Caesium Fluoride with ^{18}F- or ^{14}C-Labelled Carbonyl Fluoride and with ^{14}C-Labelled Carbon Dioxide.—Determination of the ^{18}F growth curve for the reaction of activated CsF with ^{18}F-labelled carbonyl fluoride at room temperature, Figure 4, indicated that the ^{18}F activity in the solid increased rapidly over the first 30 min of reaction and that it increased more slowly thereafter. Specific ^{18}F count rates of ^{18}FFCO before and after reaction were significantly different, Table 3, as a result of ^{18}F exchange. The count rates from the solid after removal of gas were too large to be accounted for solely by exchange, suggesting that uptake of ^{18}FFCO had occurred. This was confirmed by mass-balance determinations. Uptakes of F_2CO, Table 3, were estimated from the ^{18}F measurements after making allowance for the ^{18}F activity in the solid arising from exchange. The average uptake was 0.06 mmol (mmol CsF)$^{-1}$. The $[F_3CO]^-$ anion was detected by i.r. spectroscopy of the solid after reaction but there was no evidence for $[(CF_3)_2CFO]^-$.

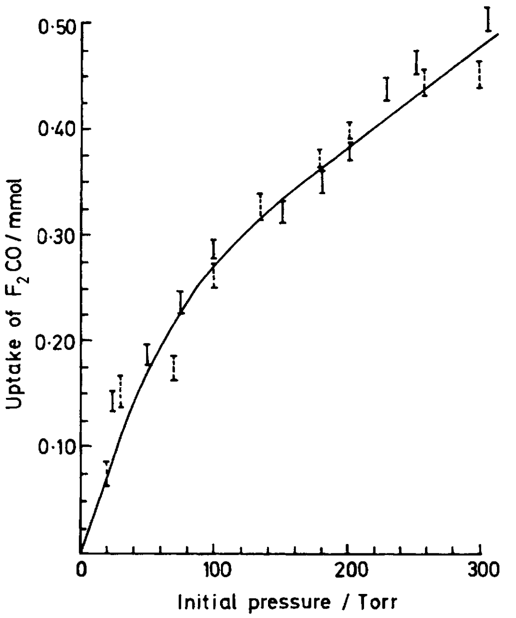

Figure 5. Relationship between the uptake of F_2CO by activated CsF (2.0 mmol) and the initial pressure of F_2CO; I, manometric measurement; ⁝, ^{14}C measurement

A small carbon-14 surface count rate was detected immediately on admission of [^{14}C]carbonyl fluoride to activated CsF. This was constant with time and independent of the initial pressure over the range 20—308 Torr. Removal of $F_2{}^{14}CO$ by pumping resulted in a barely detectable count rate indicating that >95% of the surface ^{14}C activity had been removed. Uptake of F_2CO by the bulk solid was determined both from decreases in gas-phase ^{14}C count rates of $F_2{}^{14}CO$ and manometrically, agreement between the two sets of measurements being very good. The pressure-dependent behaviour is shown in Figure 5. Approximately 46—50% of the gas taken up by activated CsF could be removed by re-evacuation of the vessel. For example the decrease in F_2CO pressure at an initial pressure of 304 Torr was equivalent to an F_2CO uptake of 0.25 mmol (mmol CsF)$^{-1}$ but that determined gravimetrically was 0.12 mmol (mmol CsF)$^{-1}$ which is closer to the value estimated from ^{18}F measurements.

The behaviour of [^{14}C]carbon dioxide towards activated CsF was similar to that of $F_2{}^{14}CO$. Admission of $^{14}CO_2$ led to a ^{14}C surface count rate that was independent of time and initial pressure over the range 25—300 Torr. Approximately 17% of the surface ^{14}C activity remained on removal of gaseous material. The maximum CO_2 uptake by the bulk solid was 0.03 ± 0.02 mmol (mmol CsF)$^{-1}$ at an initial pressure of 300 Torr. This is far smaller than that obtained for F_2CO under similar conditions and when the solid was examined by i.r. spectroscopy after reaction only the $[(CF_3)_2CFO^-]$ anion was detected.

Comparisons among the Reactions.—The formation of the anions BF_4^-, AsF_6^-, SF_5^-, and $[F_3CO]^-$ from reactions between activated CsF and the appropriate Lewis acid fluoride is not surprising since their caesium salts are well known and for example their vibrational spectra are well documented.[9,15–17] The combination of ^{35}S or ^{14}C experiments with those using ^{18}F has enabled direct evidence to be obtained for weakly bound SF_4 and F_2CO as species that are distinct from the anions and has clarified earlier work in which only ^{18}F was used.[18]

Weakly adsorbed SF_4 is the major species at the surface of activated CsF consistent with a previous suggestion[4] that it rather than the SF_5^- anion is involved in the CsF-catalysed reaction of SF_4 with ClF. The SF_5^- anion is a minor surface species but is present in the bulk. The overall reaction can therefore be represented by equation (1). The SF_5^- anion has

$$\mathrm{CsF(s)} + \mathrm{SF_4(g)} \rightleftharpoons \mathrm{CsF{\cdot}SF_4(ad)} \longrightarrow \mathrm{Cs^+SF_5^-(s)} \quad (1)$$

C_{4v} symmetry[17] and is apparently co-ordinatively saturated. It is likely that weakly adsorbed SF_4 also contains co-ordinatively saturated S^{IV} and the lack of facile ^{18}F exchange indicates that the four S–F bonds are not equivalent to that between S^{IV} and a surface F^- anion. In contrast ^{18}F exchange is observed at room temperature between $SF_3{}^{18}F$ and Lewis acids such as BF_3[19] or AlF_3.[1]

The behaviour of F_2CO towards activated CsF indicates that both surface and bulk interactions are important although weakly adsorbed F_2CO is essentially the only surface species. A possible model for the latter is provided from a matrix i.r. spectroscopic study of the reaction of CsF with formaldehyde.[20] Complete transfer of F^- anion does not occur but rather a weak interaction between F^- and the carbon atom of H_2CO as a result of which ν(CO) is shifted by 50—60 cm^{-1} compared with a shift in ν(CO) of 400 cm^{-1} when $[F_3CO]^-$ is formed from F_2CO. An analogous weak interaction between F_2CO and surface F^- anion would not obviously lead to ^{18}F exchange and it is suggested that in this case the observed exchange is the result of the reversible reactions (2).

$$\mathrm{CsF(s)} + \mathrm{F_2CO(g)} \rightleftharpoons \mathrm{CsF{\cdot}F_2CO(ad)} \rightleftharpoons \mathrm{Cs^+[OCF_3^-](s)} \quad (2)$$

The *X*-ray crystal structure of $[(Me_2N)_3S][OCF_3]$ indicates that all F atoms are equivalent but that the C–F bonds are weaker than expected. This has been rationalised on the basis of negative fluorine hyperconjugation.[21]

The carbon-14 experiments provide direct evidence for an interaction between CO_2 and the surface of activated CsF but the extent of any reaction that occurs, for example formation of the fluoroformate anion, is too small for product identification. The observed behaviour is consistent with previous lack of success in preparing caesium fluoroformate from reactions between CsF and CO_2 under various conditions,[22] although the i.r. spectrum of the matrix-isolated ion pair $Cs^+FCO_2^-$ has been reported.[23]

The order of reactivity of the Lewis acids used towards untreated CsF as measured by the extent to which permanently retained species are formed is $AsF_5 \gg BF_3 > SF_4$, Table 1, which is the same order as their fluoride-ion affinities.[24,25] The order towards CsF that has been produced by thermal decomposition of $Cs[OCF(CF_3)_2]$ is $BF_3 > AsF_5 > SF_4 \approx F_2CO > CO_2$. The fluoride affinities of SF_4 and F_2CO are similar and are more exothermic than that of CO_2,[25] but the reversal found for BF_3 and AsF_5 cannot be accounted for on a purely thermodynamic basis.

The observed order can be rationalized on the basis of fluoride-ion affinities and molecular sizes of the Lewis acids if it is assumed that activated CsF has a porous structure. The rate of reaction will depend on the degree to which the reaction occurs within the internal pore structure, the two limiting situations being that reaction occurs equally throughout the pore structure and that reaction is limited to the outside surface of individual particles.[26] In the reactions studied here differences in reaction rates will arise from differences in the molecular volumes of the Lewis acids since the CsF samples were all prepared in the same way. Arsenic pentafluoride is the strongest Lewis acid of those used but it is a relatively large molecule and reaction will be largely limited to the outside surface of CsF particles. This and the sintering that occurs during reaction are responsible for the AsF_5 uptakes being relatively small. The BF_3 molecule is smaller and can be accommodated in a wider range of pores. This and its relatively large fluoride-ion affinity result in the reaction being quantitative. Carbonyl fluoride is smaller than SF_4 and this accounts for the greater degree of reversible uptake experienced with F_2CO as compared with SF_4. Carbon dioxide should be accommodated most easily in the CsF pore structure and the very small uptakes found must be due to the very small fluoride-ion affinity of CO_2.

Experimental

All operations were carried out in Pyrex vacuum systems equipped with Monel metal pressure vessels (Hoke), an *in situ* Geiger Müller counting vessel, double-limb Pyrex counting vessels (for fluorine-18 measurements) or a constant-volume manometer. Involatile, inactive solids were transferred in a nitrogen-atmosphere glove-box (water < 10 p.p.m.). The procedures used for fluorine-18 and sulphur-35 measurements have been described previously,[1,27] and carbon-14 experiments were made using identical techniques. B.E.T. areas were determined using krypton-85 as adsorbate,[5,8] calculations being performed using a computer program that included linear regression analysis.

Activation of Caesium Fluoride.—Caesium heptafluoroisopropoxide[7] was prepared from ground caesium fluoride (26 mmol, BDH Optran grade), hexafluoroacetone (30 mmol, Fluorochem), and acetonitrile (5 cm^3, Rathburn HPLC Grade S purified as previously described[28]) by shaking the mixture in a stainless-steel pressure vessel (Hoke) at room temperature for 12 h. It was identified by its i.r. spectrum[7] and analysis (Found: C, 11.2; F, 41.5. C_3CsF_7O required C, 11.3; F, 41.8%). The solid was heated under static then dynamic vacuum at 398 K for 16 h to give an off-white solid that resembled talc in appearance. Its i.r. spectrum contained weak bands due to the $[(CF_3)_2CFO]^-$ anion (Found: C, 0.3; F, 12.4%. Molar ratio C:F = 1:27).

Carbonyl fluoride was prepared by a modified literature method[29] from carbonyl chloride (30.4 mmol, Matheson Inc.), thermally activated NaF (360 mmol), and MeCN (30 cm^3) at 293 K for 36 h in a stainless-steel pressure vessel (Hoke, 300 cm^3). Fractionation of the volatile material gave F_2CO (28.8 mmol) identified by its i.r. spectrum.[30] Caesium trifluoromethoxide[9] was prepared from F_2CO (15 mmol), ground CsF (13 mmol), and MeCN (5 cm^3) as described above and was identified by its i.r. spectrum.[9] Thermal decomposition of $Cs[OCF_3]$ under vacuum at 393 K for 3 h gave CsF of similar appearance to that obtained from $Cs[OCF(CF_3)_2]$ decomposition but bands due to the $[CF_3O]^-$ anion were not observed.

Preparation of Labelled Compounds.—Fluorine-18 was prepared in the Scottish Universities Research Reactor, East Kilbride using the sequence $^6Li(n,\alpha)^3H$, $^{16}O(^3H,n)^{18}F$ and Li_2CO_3 (2 g) as target.[31] Irradiation conditions were 3×10^{12} n cm^{-2} s^{-1} for 30 min. The $Li{}^{18}F$ produced was converted into $H^{18}F$ by distillation with 50% H_2SO_4, the distillate being trapped in aqueous CsOH at 273 K. The solution was neutralized with aqueous HF and evaporated to give finely divided solid Cs^{18}F (40—65 μCi). This was dried in a Monel metal vessel (95 cm^3) at 393 K *in vacuo* for 0.5 h. After cooling, $(CF_3)_2CO$ (10 mmol) was added and the mixture allowed to react at room temperature for 0.5 h. After removal of unchanged $(CF_3)_2CO$, the vessel was heated *in vacuo* at 393 K for 0.5 h to decompose the adduct. Treatment of Cs^{18}F in this way resulted in a significantly greater degree of ^{18}F incorporation during subsequent labelling reactions.

Arsenic pentafluoride (Ozark-Mahoning) and boron trifluoride (Matheson) were purified by low-temperature trap-to-trap distillation over thermally activated NaF before use. These fluorides and F_2CO were labelled by exchange with Cs^{18}F in a Monel metal vessel (95 cm^3), optimum conditions being 1 h, initial pressure 1 000 Torr at 398 K (for AsF_5) or at 373 K (for BF_3 and F_2CO). The fluorides were counted as solutions of their adducts in MeCN (for BF_3 and AsF_5) or at 77 K. In each case linear relationships between the count rates and quantity of sample were obtained and the radiochemical purity was established by the γ-ray spectrum and ^{18}F half-life determination.

The exchange reaction between BF_3 and Cs^{18}F (6 mmol) resulted in significant retention (*ca.* 6 mmol) of BF_3 as the BF_4^- anion. Similar observations were made with AsF_5 or F_2CO although formation of AsF_6^- or $[F_3CO]^-$ was less marked. The behaviour observed was consistent with a two-stage process involving the formation of a complex fluoro-anion followed by ^{18}F exchange between the anion and the volatile fluoride.

^{18}F Labelled sulphur tetrafluoride prepared by ^{18}F exchange with Cs^{18}F had a relatively low specific count rate and it was therefore prepared from inactive SF_4 (Matheson Inc.) and $BF_2{}^{18}F$ *via* the adduct $[SF_3][BF_4]$,[32] formation of which was responsible for complete ^{18}F exchange between $BF_2{}^{18}F$ and SF_4 at room temperature.[19] ^{18}F-Labelled SF_4 was liberated from the adduct at 193 K by adding a measured quantity of dried diethyl ether and $SF_3{}^{18}F$ was counted as a solution of its adduct in dried pyridine.

^{35}S-Labelled SF_4 was prepared as previously described,[33] and was diluted with inactive SF_4 to give a working specific count rate of 258 ± 3 count s^{-1} mmol^{-1} in the *in situ* Geiger Müller counting vessel. ^{14}C-Labelled F_2CO was prepared as described above from $Cl_2{}^{14}CO$ (1 mCi, Amersham International) diluted with inactive Cl_2CO (80 mmol). Its specific count rate was 135 ± 2 count s^{-1} mmol^{-1}. ^{14}C-Labelled carbon-dioxide was prepared from $Ba^{14}CO_3$ (1 mCi, Amersham International) and dilute acid. It was dried by three treatments with P_2O_5 for several hours and diluted with dried, inactive CO_2 to give a working count rate of 2150 ± 5 count s^{-1} mmol^{-1}. For all ^{35}S- and ^{14}C-labelled gases linear relationships of count rate *vs.* pressure were obtained.

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References

1 Part 11, K. W. Dixon, M. F. Ghorab, and J. M. Winfield, *J. Fluorine Chem.*, 1987, **37**, 357.

2 S. Katz, *Inorg. Chem.*, 1964, **3**, 1598; 1966, **5**, 666; J. G. Malm, H. Selig, and S. Siegel, *ibid.*, p. 130.

3 C. T. Ratcliffe and J. M. Shreeve, *Inorg. Synth.*, 1968, **11**, 194.

4 G. A. Kolta, G. Webb, and J. M. Winfield, *Appl. Catal.*, 1982, **2**, 257.

5 G. A. Kolta, G. Webb, and J. M. Winfield, *J. Fluorine Chem.*, 1979, **14**, 331.

6 I. Sheft, H. H. Hyman, R. M. Adams, and J. J. Katz, *J. Am. Chem. Soc.*, 1961, **83**, 291.

7 M. E. Redwood and C. J. Willis, *Can. J. Chem.*, 1967, **45**, 389.

8 D. W. Aylmore and W. B. Jepson, *J. Sci. Instrum.*, 1961, **38**, 156.

9 M. E. Redwood and C. J. Willis, *Can. J. Chem.*, 1965, **43**, 1893; K. O. Christie, E. C. Curtis, and C. J. Schack, *Spectrochim. Acta, Part A*, 1975, **31**, 1035.

10 S. J. Gregg and K. S. W. Sing, 'Adsorption, Surface Area and Porosity,' 2nd edn., Academic Press, London, 1982.

11 M. M. Dubinau, *Chem. Rev.*, 1960, **60**, 235.

12 S. J. Gregg and J. F. Langford, *Trans. Faraday Soc.*, 1969, **65**, 1394.

13 R. J. Gillespie, J. S. Hartman, and M. Parekh, *Can. J. Chem.*, 1968, **46**, 1601.

14 K. W. Dixon and J. M. Winfield, *J. Fluorine Chem.*, 1985, **29**, 355.

15 G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.

16 N. N. Greenwood, *J. Chem. Soc.*, 1959, 3811.

17 K. O. Christie, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 1972, **11**, 1679.

18 C. J. W. Fraser, D. W. A. Sharp, G. Webb, and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 1972, 2226; C. J. W. Fraser, D. W. A. Sharp, R. A. Sule, G. Webb, and J. M. Winfield, *J. Chem. Res.*, (*S*) 1978, 2; (*M*) 1978, 0311.

19 M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 1969, **47**, 4159.

20 S. B. H. Bach and B. S. Ault, *Inorg. Chem.*, 1984, **23**, 4394.

21 W. B. Farnham, B. E. Smart, W. J. Middleton, J. C. Calabrese, and D. A. Dixon, *J. Am. Chem. Soc.*, 1985, **107**, 4565 and refs. therein.

22 L. Lawlor and J. Passmore, *Inorg. Chem.*, 1979, **18**, 2923.

23 B. S. Ault, *Inorg. Chem.*, 1982, **21**, 756.

24 T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco, and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167.

25 J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, 1985, **107**, 766; *Inorg. Chem.*, 1987, **26**, 4018.

26 See, for example, R. H. Borgwardt and R. D. Harvey, *Environ. Sci. Technol.*, 1972, **6**, 350.

27 D. K. Sanyal and J. M. Winfield, *J. Fluorine Chem.*, 1984, **24**, 75.

28 J. M. Winfield, *J. Fluorine Chem.*, 1984, **25**, 91.

29 F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, 1962, **84**, 4275.

30 P. D. Mallinson, D. C. McKean, J. H. Holloway, and I. A. Oxton, *Spectrochim. Acta, Part A*, 1975, **31**, 143.

31 J. E. Whitley, Scottish Research Reactor Centre Report No. 26/68, East Kilbride, 1968.

32 D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 1972, **11**, 2325.

33 G. A. Kolta, G. Webb, and J. M. Winfield, *J. Fluorine Chem.*, 1981—1982, **19**, 89.

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