*Journal of Fluorine Chemistry*, *37* (1987) 357–370

Received: April 9, 1987; accepted: August 9, 1987

# RADIOTRACERS IN FLUORINE CHEMISTRY, PART XI. THE BEHAVIOUR OF [$^{18}$F]-FLUORINE AND [$^{35}$S]-SULPHUR LABELLED SULPHUR TETRAFLUORIDE AT LEWIS ACID FLUORIDE SURFACES [1]

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## SUMMARY

The behaviour of sulphur tetrafluoride towards solid aluminium(III), chromium(III), niobium(V), and tantalum(V) fluorides at room temperature has been determined using $SF_4$ labelled with [$^{18}$F]-fluorine or [$^{35}$S]-sulphur. Isolable adducts are not formed, but adsorption of $SF_4$ and exchange of $^{18}F$ do occur. It is proposed that the adsorbed species is a pyramidal trifluorosulphur group bound by weak fluorine bridges to the metal fluoride surface in the case of $AlF_3$ or $CrF_3$, and to fluorometallate(V) anions in the case of niobium(V) or tantalum(V) fluorides. A re-examination of the behaviour of $^{35}SF_4$ towards β-uranium pentafluoride is consistent with the latter behaving as a Lewis acid. Uptake of $SF_4$ is small but it is irreversible. Evidently the interaction is stronger than with the other fluorides studied.

## INTRODUCTION

In previously reported radiotracer work from this laboratory it has been shown that sulphur tetrafluoride interacts with a caesium fluoride surface to form weakly adsorbed $SF_4$ and irreversibly bound $SF_5^-$ [2a]. The existence of the solid compound $Cs^+SF_5^-$ is well documented in the literature, for example [2b], and it has been established from a study of its vibrational spectrum that the $SF_5^-$ anion has $C_{4v}$ symmetry [2c]. It is weakly adsorbed $SF_4$ however that is important in the CsF catalysed chlorofluorination of $SF_4$ by chlorine monofluoride, as the reaction between $SF_5^-$ and ClF is very much slower than that between surface-adsorbed $SF_4$ and ClF [3].

0022-1139/87/$3.50

The ability of $SF_4$ to behave as a fluoride ion donor is equally well documented. There have been several reports describing complex formation between $SF_4$ and Lewis acid fluorides such as boron trifluoride, phosphorus pentafluoride, arsenic pentafluoride, and antimony pentafluoride [4]. The vibrational spectra of these compounds have been interpreted on the basis of ionic structures $[SF_3^+][BF_4^-]$ or $[SF_3^+][MF_6^-]$, M = P, As, or Sb, with relatively strong fluorine bridging between the ions. This has been confirmed for $[SF_3^+][BF_4^-]$ by X-ray crystallography [5]. Similarly the X-ray crystal structure of $2SF_4.GeF_4$ indicates that this compound is $[SF_3^+]_2[GeF_6^{2-}]$ with fluorine bridging between anion and cation [6].

Aluminium and chromium trifluorides are usually regarded as weak Lewis acids, but the possible acidities of metal(III) sites on the surfaces of these solids are very relevant to the investigation of their catalytic properties [1,7,8]. A study of $[^{18}F]$-fluorine exchange between $SF_4$ and $BF_3$ has been reported [4] and we wished to determine whether radiotracer techniques using $[^{18}F]$-fluorine and $[^{35}S]$-sulphur could be used to demonstrate $SF_4$ adsorption at $AlF_3$ and $CrF_3$ surfaces. Although isolable adducts have not been described for these systems, the formation of $SF_3^+$ at the surface is an attractive possibility.

A similar approach has been used to investigate the behaviour of $[^{35}S]$-sulphur labelled $SF_4$ towards β-uranium pentafluoride, a system in which $[^{18}F]$-fluorine exchange has been demonstrated previously [9]. The results of a study of interactions occurring between $[^{35}S]$-sulphur and $[^{18}F]$-fluorine labelled $SF_4$ and solid niobium and tantalum pentafluorides are also reported. In these systems the structurally characterized selenium tetrafluoride, metal pentafluoride complexes [10] are helpful analogies in interpreting the observed behaviour.

These systems all have features in common, although they differ in detail due to the different physical properties of the Lewis acid fluorides.

## RESULTS AND DISCUSSION

### The Interaction of Sulphur Tetrafluoride with Aluminium and Chromium Trifluorides

Admission of $[^{18}F]$-labelled $SF_4$ to solid, anhydrous $AlF_3$ or $CrF_3$ samples at room temperature results in the incorporation of $^{18}F$ in the solids. With $AlF_3$ the growth in radioactivity is rapid during the first 30 min; thereafter a constant count rate is observed, Fig. 1. The growth of $^{18}F$ activity in $CrF_3$ is less pronounced and a constant count rate is not observed even after 60 min.

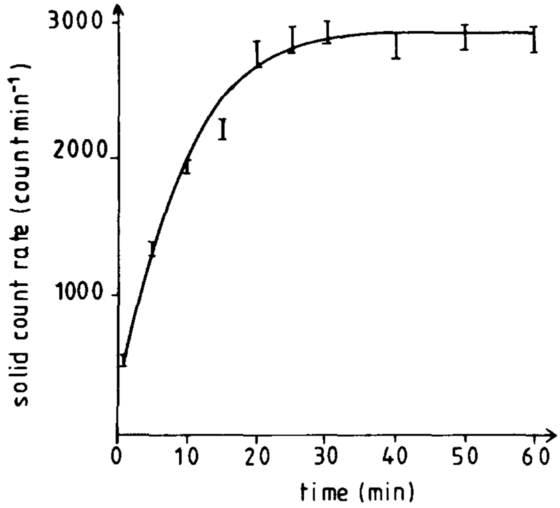

Fig. 1. Variation of $^{18}F$ count rate in $AlF_3$ with time after exposure to $SF_3{}^{18}F$ (initial pressure 300 Torr).

The $^{18}F$ activity observed in both solids arises from $^{18}F$ exchange with $SF_3{}^{18}F$. The fraction of activity exchanged (f), determined on removal of $SF_3{}^{18}F$ after 60 min exposure and defined as the fraction of $^{18}F$ in the solid divided by the fraction of the total fluorine in the solid, is greater for $AlF_3$ than for $CrF_3$.
Typical results are shown in Table 1 (over).

TABLE 1

Room temperature $^{18}F$ exchange between $SF_3{}^{18}F$ and $AlF_3$ or $CrF_3$

| $MF_3$ mmol | $SF_3{}^{18}F$ mmol$^a$ | Specific count rate of $SF_3{}^{18}F$ count min$^{-1}$mmol$^{-1}$ | | fraction of $^{18}F$ exchanged |
|---|---|---|---|---|
| | | initial | after 60 min | |
| 5.95 (Al) | 1.0 | 12326 ± 111 | 9274 ± 96 | 0.30 ± 0.01 |
| 5.95 (Al) | 1.0 | 5627 ± 75 | 4160 ± 64 | 0.31 ± 0.01 |
| 5.4 (Cr) | 1.0 | 46697 ± 216 | 41604 ±204 | 0.18 ± 0.01 |

$^a$Initial pressure of $SF_4$ = 300 Torr.

[$^{35}S$]-Sulphur activity is detected immediately from $AlF_3$ and $CrF_3$ samples when the solids are exposed to [$^{35}S$]-$SF_4$ at room temperature. The count rates do not change with time but decrease rapidly to background when gaseous $^{35}SF_4$ is removed. The magnitude of the $^{35}S$ solid count rate depends on the pressure of $^{35}SF_4$ in the system and was investigated in detail for $AlF_3$, with the results shown in Figs. 2 and 3. The detection of $^{35}S$ activity in a solid is limited to its surface because of $^{35}S$ ($\beta^-_{max}$= 0.167 MeV) self-absorption, and Fig. 2 indicates that for $SF_4$ initial pressures of up to 300 Torr saturation coverage of the $AlF_3$ surface is not achieved. A similar relationship is observed between the total uptake of $SF_4$ by $AlF_3$ and the initial pressure of $SF_4$, Fig. 3. This was determined in two ways, from the decrease in $^{35}S$ activity in the gas phase and by measuring pressure decrease manometrically. The uptakes of $SF_4$ by $CrF_3$ are smaller than those observed for $AlF_3$ in Figure 3, for example at a 300 Torr initial pressure of $SF_4$ the uptake by $CrF_3$ is approximately 0.01 mmol (mmol $CrF_3$)$^{-1}$. In other respects the behaviour of the two fluorides is very similar.

We conclude that the interaction of $SF_4$ is limited to the metal fluoride surface in both cases. Aluminium and chromium trifluorides have structures in which the fluorine lattice is intermediate between cubic and hexagonal close-packed arrays with the metals occupying octahedral holes [11,12]. It is likely therefore that their surfaces will contain coordinatively unsaturated metal(III) centres which will behave as Lewis acid sites. The X-ray crystal

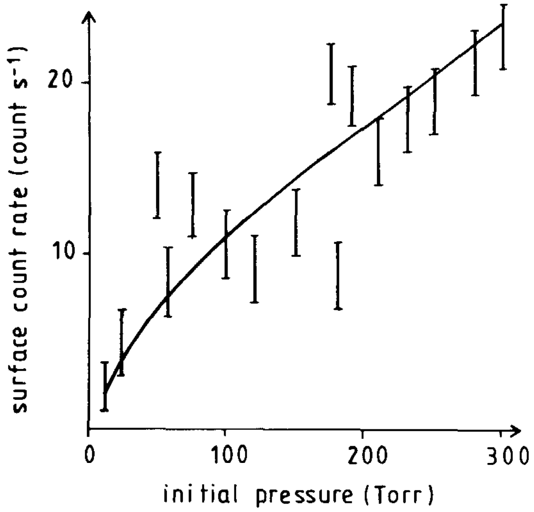

Fig. 2. Variation of $^{35}SF_4$ surface count rate on $AlF_3$ with initial $SF_4$ pressure.

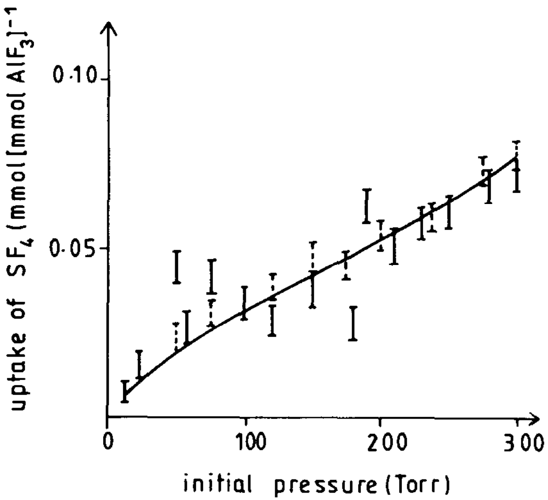

Fig. 3. Variation of $SF_4$ uptake by $AlF_3$ with initial $SF_4$ pressure. I Determined from decrease in $^{35}SF_4$ gas phase counts. ⁞ Determined manometrically.

structures of the adducts $SF_4.BF_3$ and $2SF_4.GeF_4$ indicate that sulphur has a distorted octahedral environment, consistent with the presence of trifluorosulphur(+1) cations of $C_{3v}$ symmetry making three close contacts with fluorine atoms from neighbouring $BF_4^-$ or $GeF_6^{2-}$ anions [5,6]. Such an arrangement appears to be characteristic for chalogen(IV) halide adducts with Lewis acid halides [10,13], and it leads to a model for the weakly adsorbed surface species observed in the present work. We propose that $SF_4$ molecules are weakly coordinated to surface metal(III) centres via a fluorine bridge with two additional secondary bonds being formed to sulphur from adjacent fluorines on the surface. The interaction is obviously weaker than those present in isolable $SF_3^+$ complexes [5,6], but it provides a mechanism for the $^{18}F$ exchange observed. It would be expected that exchange would be limited to fluorines at or near the surface and this is consistent with the relatively small values of f (Table 1) which are observed. The larger uptake of $^{35}SF_4$ and the larger value of f observed with $AlF_3$ are consequences of its larger surface area compared to that of $CrF_3$. The B.E.T. surface area determined for the $AlF_3$ used in this work is 22.3 ± 2.6 $m^2g^{-1}$ compared to a value of approximately 5 $m^2g^{-1}$ determined for $CrF_3$.

## The Interaction of Sulphur Tetrafluoride with Niobium and Tantalum Pentafluorides

Admission of $[^{18}F]$-labelled $SF_4$ to solid niobium or tantalum pentafluorides at room temperature leads to incorporation of $^{18}F$ in the solids. The $^{18}F$ growth curves are essentially identical in shape to that depicted for the $SF_3{}^{18}F$,$AlF_3$ system in Fig. 1, however $^{18}F$ exchange is complete after 50 min, Table 2.

TABLE 2

Room temperature $^{18}F$ exchange between $SF_3{}^{18}F$ and niobium(V) or tantalum(V) fluorides

| $MF_5$ mmol | $SF_3{}^{18}F$ mmol[a] | Specific count rate of $SF_3{}^{18}F$ count $min^{-1}$ $mmol^{-1}$ | | fraction of $^{18}F$ exchanged |
|---|---|---|---|---|
| 2.7 (Nb) | 1.0 | 15768 ± 125 | 2762 ± 53 | 1.06 ± 0.01 |
| 2.7 (Nb) | 1.0 | 9765 ± 99 | 2239 ± 47 | 0.99 ± 0.01 |
| 6.9 (Ta) | 1.0 | 16316 ± 128 | 5410 ± 74 | 1.00 ± 0.01 |

[a] Initial pressure of $SF_4$ = 300 Torr

The interaction between [$^{35}$S]-$SF_4$ and niobium pentafluoride at room temperature was examined using ten different initial pressures of $SF_4$ in the range 25 to 305 torr. In each case the $^{35}$S count rate at the surface increases over the initial 20-25 min of the experiment, thereafter it decreases until it becomes essentially constant after 60 min. This time corresponds to the observation of complete $^{18}$F exchange. At low initial pressures of $SF_4$ the maximum value of the surface $^{35}$S count rate is very small, but it increases with increasing initial pressure, and is constant at pressures greater than 100 Torr. The relationship between surface count rate and time for an initial pressure of 305 Torr is shown in Fig. 4.

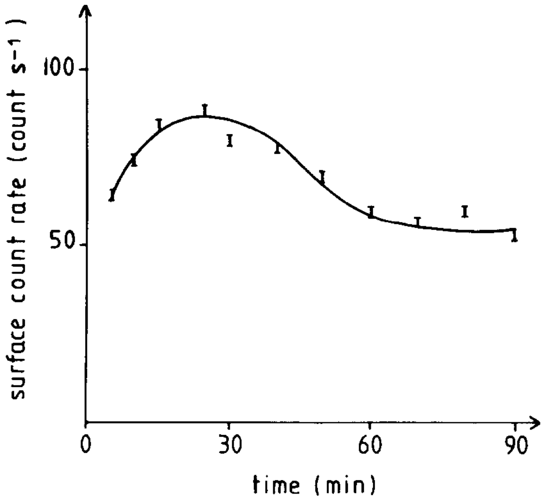

Fig 4. Variation of $^{35}$S surface count rate on niobium pentafluoride with time. Initial pressure of $SF_4$ = 305 Torr.

During these experiments the walls of the counting vessel became coated with a thin layer of off-white solid which is ascribed to trace hydrolysis of pentafluoride on the Pyrex wall.

Removal of $^{35}SF_4$ from the gas phase results in the surface $^{35}$S count decreasing to background. Admission of further $^{35}SF_4$ leads to behaviour identical to that described above except that a barely significant $^{35}$S surface count is detected after $^{35}SF_4$ removal. The behaviour observed in the $^{35}SF_4$, tantalum pentafluoride system appears to be identical although it was studied in less detail.

These experiments indicate that a surface species is formed, but that the nature of that species or of the metal pentafluoride surface, changes during the course of the reaction. It is considered that initially $SF_4$ is weakly adsorbed at the pentafluoride surface but further reaction occurs to give $[SF_3^+][M_2F_{11}^-]$ or $[SF_3^+][MF_6^-]$, M = Nb or Ta, analogous to $[SeF_3^+][Nb_2F_{11}^-]$ or $[SeF_3^+][MF_6^-]$, M = Nb or Ta [10]. The surface complexes formed apparently exist only in equilibrium with gaseous $SF_4$ and solid $(MF_5)_4$ [14] or pentafluoride vapour. The latter at room temperature is likely to be predominantly trimeric, $(MF_5)_3$ [15]. A rapidly established equilibrium between the surface complex and its constituent fluorides, coupled with the equilibrium between solid pentafluorides and their vapours, would account for the complete exchange of $^{18}F$ observed at room temperature. A related situation exists in the $SF_4$, $BF_3$, $[SF_3^+][BF_4^-]$ system in which the complete $^{18}F$ exchange observed at room temperature has been accounted for by the reversible dissociation of solid $[SF_3^+][BF_4^-]$ [4]. Direct $^{18}F$ exchange between $SF_3{}^{18}F$ and $(MF_5)_3$ in the gas phase is another possibility, although it is not necessary to invoke this in order to account for the observed behaviour.

## The Interaction of Sulphur Tetrafluoride with β-Uranium Pentafluoride

Exposure of β-uranium pentafluoride to $[^{35}S]$-$SF_4$ at room temperature leads to the immediate detection of a $^{35}S$ surface count rate which does not change with time but, unlike the behaviour encountered with $AlF_3$ and $CrF_3$, is unaffected by removal of gaseous $^{35}SF_4$. Admission of inactive $SF_4$ also has no effect. The surface count rate is strongly dependent on the initial pressure of $SF_4$ below 200 Torr but above this it is essentially independent, Fig. 5.

The magnitude of the uptake of $SF_4$ by β-$UF_5$, determined from the decrease in gas phase $^{35}SF_4$ count rate at the saturation surface coverage, is approximately 0.27 mmol (mmol $UF_5$)$^{-1}$. Evidently the reaction between the two compounds is not limited to the surface of β-$UF_5$ and, perhaps fortuitously, the combining ratio is not too dissimilar from that of the solid $3UF_5.SF_4$ which has been isolated from the reaction of $SF_4$ with $UF_5$ in anhydrous HF [16]. This adduct has been formulated as $[SF_3^+][UF_6^-].2UF_5$.

In an earlier radiotracer study of the $SF_4$, β-$UF_5$ system substantial $^{18}F$ exchange was observed under heterogenous conditions, f being 0.70 after 120 min, and retention of $^{35}SF_4$ was observed [9]. By analogy with the retention of $SF_4$ by a caesium fluoride surface [3] and bearing in mind the fluorine-donor properties of $UF_5$ in many of its adducts with strong Lewis acid fluorides [16,17], it was suggested that $SF_4$ is retained at Lewis base sites on the surface of β-$UF_5$.

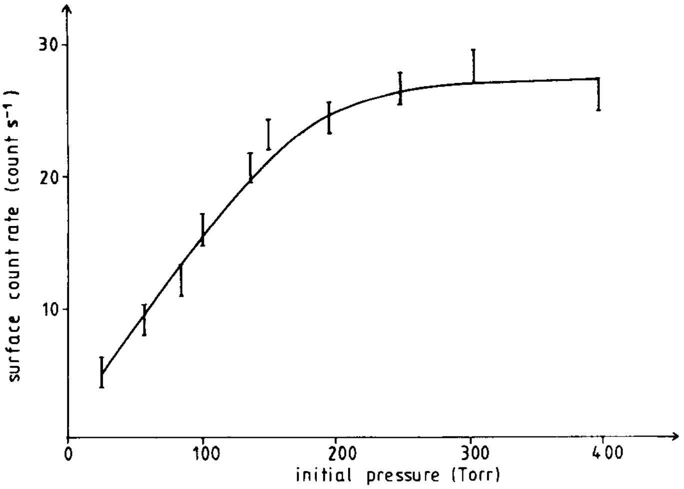

Fig. 5. Variation of $^{35}S$ surface count rate on β-$UF_5$ with initial pressure of $SF_4$.

Subsequently it has been shown that neither weakly adsorbed or strongly bound $SF_4$ undergo observable $^{18}F$ exchange with CsF at room temperature [2a]. Because of this, and in view of the behaviour of $SF_4$ towards $AlF_3$ and $CrF_3$, it now appears more likely that $SF_4$ behaves as a Lewis base towards a β-$UF_5$ surface, in agreement with synthetic experience [16].

The observation of irreversible adsorption of $SF_4$ at the β-$UF_5$ surface is presumably a consequence of stronger fluorine bridging between $SF_4$, or $SF_3^+$, and the surface. However the relationship between the formation of a bound complex and the considerable exchange of $^{18}F$ which is observed has not been determined.

## CONCLUSION

This work has shown that the behaviour of sulphur tetrafluoride towards solid Lewis acid fluorides can be described using a combination of [$^{18}F$]-fluorine and [$^{35}S$]-sulphur radiotracers. The strength of the interaction depends on the nature of the surface but significant $^{18}F$ exchange is observed in all cases. This distinguishes $SF_4$ behaviour to Lewis acids from its behaviour towards caesium fluoride, and reflects the different fluorine-environments for sulphur(IV) in the two situations.

## EXPERIMENTAL

All operations were carried out in a Pyrex vacuum line or in a $N_2$-atmosphere glove box ($H_2O$ < 10 p.p.m.). Aluminium trifluoride (Ozark Mahoning, stated purity 99.5%) and chromium trifluoride (Fluorochem Ltd.) were stored in the glove box and were used as received. Niobium and tantalum pentafluorides (Fluorochem Ltd.) were sublimed *in vacuo* immediately before use. β-Uranium pentafluoride was prepared by reduction of uranium hexafluoride (British Nuclear Fuels plc) by molecular iodine in iodine pentafluoride (Fluorochem Ltd.) [18]. Sulphur tetrafluoride was prepared by the reaction of $IF_5$ with elemental sulphur [19].

### [$^{18}$F]-Fluorine Studies

Methods for the production of the [$^{18}$F]-labelled compounds, caesium fluoride and sulphur tetrafluoride and for the determination of $^{18}$F count rates have been described previously [9]. The interaction of $SF_3{}^{18}F$ with the solid fluorides were studied using a double limbed, H-shaped Pyrex vessel, volume *ca.* 60 $cm^3$, fitted with P.T.F.E./Pyrex stop-cocks (J. Young Ltd.). Each limb fitted into the well scintillation counter and gave identical count rates when filled with $SF_3{}^{18}F$. The relationship between count rate and pressure of $SF_4$ was linear.

The following experimental procedure was used. A weighed quantity, usually 1-3 mmol, of the solid fluoride was placed in one limb of a previously evacuated, flamed-out counting vessel, in the glove box. The vessel was transferred to the vacuum line, pumped for 30 min, and a measured pressure of $SF_3{}^{18}F$ admitted. The material in each limb was counted alternately at regular intervals over 1-2 h. Counts from the limb containing the solid were due to $^{18}$F incorporated in the solid plus gaseous $SF_3{}^{18}F$, while counts from the other limb arose from $SF_3{}^{18}F$ alone. Subtraction of the latter from the former gave the count due to the solid. These data, corrected for $^{18}$F decay and background, were used to obtain count rate vs. time relationships, for example Figure 1. When no further increase in the solid count rate was observed $SF_3{}^{18}F$ was removed by vacuum distillation and counted in a single limb counting vessel containing a small quantity of pyridine. The solid was counted also. Radiochemical balances were > 95% with respect to an aliquot of $SF_3{}^{18}F$ counted in pyridine at the start of the experiment. In separate experiments it was established that the variation between the count rate and mass of $SF_3{}^{18}F$ was linear.

The results from these experiments, Tables 1 and 2, were used to determine the fraction of $^{18}F$ activity exchanged (f). This was calculated in two ways, equations (1) and (2).

$$f = \frac{A_1}{A_1 + A_2}\left(\frac{xm_1}{xm_1 + 4m_2}\right)^{-1} \qquad (1)$$

$$f = \frac{S_o - S_t}{S_o - S_\infty} \qquad (2)$$

$A_1$ and $A_2$ count $s^{-1}$ are the count rates, corrected for decay and background, of the solid fluoride and $SF_3{}^{18}F$ respectively, after exchange between $m_1$ mmol of solid fluoride containing x fluorine atoms and $m_2$ mmol of $SF_3{}^{18}F$. $S_o$, $S_t$, and $S_\infty$ are specific count rates (count $s^{-1}mmol^{-1}$) of $SF_3{}^{18}F$ prior to exchange, after exchange, and calculated if exchange were to be complete. Provided that $SF_3{}^{18}F$ is not permanently retained by the solid fluoride, f values calculated from eqns. (1) and (2) are identical. This was shown to be the case for experiments involving $AlF_3$, $CrF_3$, $(NbF_5)_4$, and $(TaF_5)_4$.

## [$^{35}S$]-Sulphur Studies

The design of the counting vessel was based on that used for the study of adsorption of [$^{14}C$]-carbon labelled hydrocarbons at supported metal catalysts [20]. Two Geiger Müller counters (Mullard ZP1481) were mounted side by side within an evacuable Pyrex vessel which was equipped with a vertically mounted ampoule from which a solid fluoride could be delivered into a moveable Pyrex boat contained within the vessel. The boat could be positioned so that the solid would be directly under one tube. This arrangement ensured that one counter would detect $^{35}S$ activity originating only from the gas phase, while the other detected activity from the solid surface and from the gas above.

The counting vessel was connected to a gas-handling manifold equipped with P.T.F.E./Pyrex stop cocks and the apparatus was calibrated. In order to ensure that counting geometries of the Geiger Müller counters were identical, care was taken to ensure that the distances from the end window to the boat were identical. A [$^{137}Cs$]-caesium source was used to verify equal counting geometries. The counters were intercalibrated by determining count rates from [$^{35}S$]-labelled $SF_4$ over the pressure range 10-300 Torr. Labelled $^{35}SF_4$ was prepared from [$^{35}S$]-labelled rhombic sulphur (1mCi, Amersham International) and $IF_5$ [19]. Count rate vs. pressure relationships were linear and the intercalibration factor was obtained from the gradient of the plot of counter 1 vs. counter 2. Deadtimes of the counters and their scalers (Nuclear Enterprises SR7) were determined by following the decay of $Cs^{18}F$ over several half-lives.

The following experimental procedure was used. The ampoule, previously evacuated and flamed out, was loaded with a solid fluoride, usually 1-3 mmol, in the glove box. The ampoule was re-evacuated and attached to the counting vessel which was then pumped for at least 30 min. A measured pressure of $^{35}SF_4$ was admitted to the vessel and its count rate (error < ± 1%) determined. The $^{35}SF_4$ was removed by condensation in a storage bulb attached to the manifold, the solid fluoride admitted to the boat, and the latter positioned under one counter. The $^{35}SF_4$ was readmitted to the vessel and the count rates from gas and from gas-plus-solid determined at regular intervals until count rates were constant. Counting times at equilibrium were chosen to ensure radiochemical errors < ± 1%. Subtraction of gas from gas-plus-solid count rates, after correction for deadtime, background and intercalibration, gave $^{35}S$ count rates at the surface of the solid fluoride. These were constant with time for a given pressure of $SF_4$ except for niobium and tantalum pentafluorides, Fig. 4.

The above sequence of operations was repeated over a range of $^{35}SF_4$ pressures and plots of $^{35}S$ surface count rate vs. initial pressure of $SF_4$ were obtained, Figures 2 and 5. The uptake of $SF_4$ by a solid fluoride was determined at each initial pressure of $SF_4$ used, from the decrease in gas phase $^{35}SF_4$ count rate observed at equilibrium together with the $^{35}SF_4$ count rate vs. $SF_4$ pressure relationship. The validity of this approach was checked for $AlF_3$ by measuring decreases in pressure resulting from the interaction using a small dead-space manifold and a constant volume manometer. The agreement between the two techniques was good, Fig. 3.

There was no evidence for hydrolysis in these experiments except in those involving niobium and tantalum pentafluorides when the walls of the vessel, which could not be adequately flamed out, became coated with a thin layer of solid during an experiment. This was presumably due to trace hydrolysis of pentafluoride vapour by adsorbed water but the quality of the radiochemical data was not affected.

## ACKNOWLEDGEMENTS

We thank the reactor staff at the S.U.R.R.C., East Kilbride for assistance with neutron irradiations, British Nuclear Fuels, plc, for a gift of $UF_6$, and the University of Glasgow and the Government of Algeria respectively, for financial awards to K.W.D. and M.F.G.

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