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PRELIMINARY NOTE

Surface Complexation by Caesium Fluoride. The Case of Sulphur Tetrafluoride

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SUMMARY

The heterogeneous, room temperature complexation reaction between caesium fluoride and sulphur tetrafluoride is conveniently observed using ^{18}F and ^{35}S radiotracer methods. The major surface species is weakly adsorbed SF_4, SF_5^- being a minor species. Neither undergo observable ^{18}F exchange with CsF at room temperature.

The widespread use of caesium fluoride as a catalyst under heterogeneous conditions implies the existence of reactive, adsorbed species. For example a reaction scheme for the catalytic chlorofluorination of sulphur tetrafluoride proposed from a sulphur - 35 and chlorine - 36 radiotracer study [1], involves SF_4 and ClF weakly adsorbed at CsF. A more detailed examination of SF_4 adsorption is now presented.

Room temperature interactions between CsF, activated by formation and subsequent thermal decomposition of its 1:1 adduct with hexafluoroacetone to increase its surface area [2], and $[^{35}S]$ - SF_4 or $[^{18}F]$ - SF_4 have been studied by direct monitoring Geiger-Müller or well-scintillation counting techniques respectively. These enable increases in radioactivity of the solid phase during reactions to be followed [1, 3]. Results using the two tracers are complementary. ^{18}F (0.51 MeV γ) activity observed in CsF could arise from ^{18}F exchange

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and from uptake of $SF_3{}^{18}F$ by both surface and bulk CsF. Observation of ^{35}S activity in CsF is limited to its surface due to $^{35}S(\beta^-max = 0.167\ MeV)$ self-absorption. However uptake of $^{35}SF_4$ by surface and bulk can be determined indirectly from the decrease in gaseous ^{35}S count rate during a reaction. Using $SF_3{}^{18}F$ and $^{35}SF_4$ of measured specific count rates enable stoicheimetries to be precisely determined more easily than by conventional manometric methods.

At pressures greater than 10 Torr saturation coverage of CsF by $^{35}SF_4$ is observed, (Fig. 1.) 85% of the surface activity is removed rapidly when gaseous $^{35}SF_4$ is removed by condensation, and this must be due to weakly adsorbed $^{35}SF_4$. The remainder cannot be desorbed by pumping at room temperature. ^{18}F activity observed in CsF during reaction with $SF_3{}^{18}F$, (Fig. 2) is virtually unaffected by removal of gaseous $SF_3{}^{18}F$. Specific count rates determined for $SF_3{}^{18}F$ before and after reaction are identical within experimental error, therefore ^{18}F in the solid arises solely from $SF_3{}^{18}F$ uptake by bulk and surface CsF. The uptake is independent of initial pressure over the range 100 - 300 Torr, and corresponds to 0.09 $\pm$0.02 mmol (mmol CsF)$^{-1}$. That determined indirectly from $^{35}SF_4$ experiments is 0.10 $\pm$ 0.02 mmol (mmol CsF)$^{-1}$.

The i.r. spectrum of the solid after treatment with SF_4 contains bands attributable to the $SF_5{}^-$ anion [4], thus it is a reasonable assumption that $SF_5{}^-$ is the major bulk species and the minor surface species. The absence of detectable ^{18}F exchange at room temperature is partly a consequence of S^{IV} in $SF_5{}^-$ being coordinatively saturated, but it also indicates that in the weakly adsorbed state, the S-F bonds of SF_4 retain their integrity. ^{18}F exchange between $Cs^{18}F$ and SF_4 is observed above 80°C and presumably occurs via an $SF_4{}^{18}F^-$ dissociative process too slow to be observed at room temperature.

The behaviour described above contrasts with that of $^{35}SF_4$ and $SF_3{}^{18}F$ towards the solid Lewis acids $(NbF_5)_4$ and AlF_3 where room temperature ^{18}F exchange with no retention is observed.

The B.E.T. surface area of CsF pretreated with $(CF_3)_2CO$, determined using ^{85}Kr as adsorbate [2] is in the range (95% confidence limits) 3.011 - 2.083 m^2g^{-1}. The maximum number of surface F^- ions in a typical CsF sample (3.30 mmol), calculated from the surface area measurements and a value of 6.008Å for the CsF unit cell edge [5],

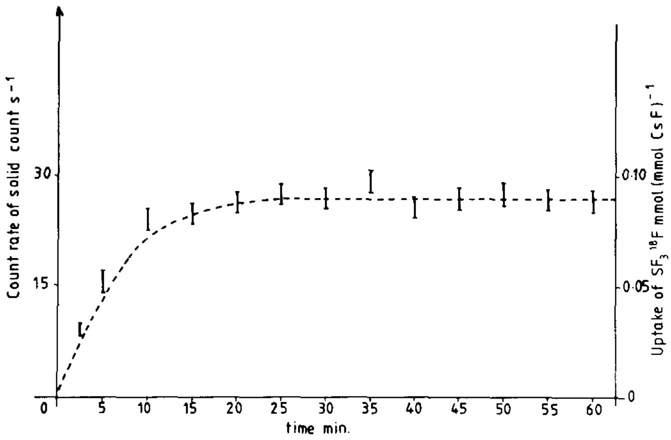

Fig. 1. Variation of $^{35}SF_4$ surface coverage with initial $^{35}SF_4$ pressure. Coverage was determined after 1h from differences between gas + solid and gas-only ^{35}S counts.

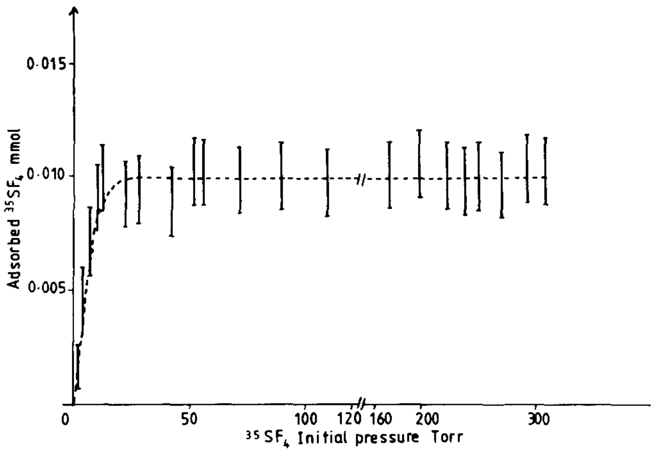

Fig. 2. Uptake of $SF_3{}^{18}F$ by CsF with time. Initial $SF_3{}^{18}F$ pressure = 300 Torr.

is in the range (5.771 - 8.342) x 10^{18}. The observed surface ^{35}S count rate corresponds to (5.99 ± 2.13) x 10^{18} molecules. Although the agreement between these two estimates is satisfactory, it does not rule out the possibilities that SF_4 is weakly adsorbed at sites other than F^- or that multiple adsorption occurs.

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