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FLUORINE-18 EXCHANGE REACTIONS INVOLVING URANIUM PENTA- AND HEXA-FLUORIDES

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Fluorine-18 exchange between UF_6 , UF_5 , or UF_6^- salts and $BF_2^{18}F$, $PF_4^{18}F$, $WF_5^{18}F$, or $Me_3Si^{18}F$ has been investigated both under heterogeneous conditions and in MeCN solution, with particular emphasis on those situations where comparisons with ligand substitution reactions of UF_6 and UF_5 can be made. In most reactions studied, essentially complete ^{18}F exchange is observed, for example those between β - UF_5 and $BF_2^{18}F$ or $Me_3Si^{18}F$ have half lives ca. 6 min. at ambient temperature. However exchange between α - UF_5 and $BF_2^{18}F$ occurs to a lesser extent. The behaviour of the β - UF_5 , $BF_2^{18}F$ system with time suggests that a surface complex is formed. β - UF_5 and UF_6^- have significant F-donor properties both in gas-solid and in solution reactions. The same is probably true for UF_6 , which is much more labile than WF_6 . The lability of U^{VI} -F and U^V -F bonds indicated from the ^{18}F exchange reactions is consistent with the lability of the recently reported derivatives $UF_{6-n}(OMe)_n$ (E.A. Cuellar and T.J. Marks, *Inorg. Chem.*, 1981, 20, 2129) and $UF_{5-n}Cl_n$ (J.A. Berry, J.H. Holloway, and D. Brown, *Inorg. Nucl. Chem. Lett.*, 1981, 17, 5), prepared for reactions of UF_6 and UF_5 with Me_3SiX , X = OMe or Cl. Insoluble $UF_3(OMe)_2$ is formed from UF_5 and Me_3SiOMe in MeCN, probably via the formation of $U(OMe)_5$ followed by ligand redistribution between $U(OMe)_5$ and UF_5 . $UF_3(OMe)_2$ undergoes ^{18}F exchange with $Me_3Si^{18}F$ but its reaction with Me_3SiOMe is very slow. Mixtures of U^V chlorofluorides, together with $(CF_3)_2CO$, are formed from UF_5 and $B[OCCl(CF_3)_2]_3$.

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HALOGEN EXCHANGE AT THE SURFACE OF FLUORINATED CHROMIUM(III) OXIDE. AN ISOTOPIC TRACER STUDY

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The chromium(III) oxide catalysed fluorination of chlorinated ethanes by hydrogen fluoride is well documented, but little is known about the nature of the surface or the substrate-catalyst interactions. We have undertaken an isotopic tracer study to obtain information in this area. The uptake of HF by catalyst samples at 350°C is considerable, and in the early stages is accompanied by the formation of a liquid product, presumed to be aqueous HF. 2H_2 catalyst exchange experiments indicate that exchangeable hydrogen, present in fresh catalyst samples as surface hydroxyl groups, is completely removed by treatment of the catalyst with HF. Fluorine-18 deposited on the catalyst using $H^{18}F$ can be partially removed at 350°C either (i) by flowing He over the catalyst, (ii) by flowing inactive HF over the catalyst, or (iii) by treatment of the catalyst with inactive HF under static conditions. The fractions of fluorine-18 retained depend on the conditions used, being (i) >85%, (ii) 30-50%, and (iii) 60-70% respectively. Flowing $C_2Cl_2F.CClF_2$ at 350°C over catalysts pretreated with HF or $H^{18}F$ results in mixtures of $C_2Cl_{2-n}F_n$, n = 2-5, as identified products, indicating that several Cl-F exchange equilibria are involved. Under the conditions used the overall reaction appears to be zero order in gaseous $C_2Cl_2F.CClF_2$. Incorporation of ^{18}F in the products is observed, but it occurs only to a relatively small extent. The implications of these observations for possible reaction mechanisms will be discussed.