Journal of Fluorine Chemistry, 53 (1991) 33–42

Received: November 22, 1990; accepted: May 30, 1991

POLYHALOAROMATIC EQUILIBRATIONS

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SUMMARY

Chromium oxide is a good catalyst for scrambling halogens among polyhaloaromatic compounds. Chloropentafluorobenzene and bromopentafluorobenzene disproportionate to hexafluorobenzene and the respective tetrafluorodihalobenzenes. Pentachloro- and pentafluoropyridines produce pyridines with intermediate numbers of both types of halogens. Cyano, trifluoromethyl and a single hydrogen can be present on the aromatic rings without interfering with the chemistry.

INTRODUCTION

Treating polychlorinated aromatics with KF in a dipolar, aprotic solvent is the preferred route to polyfluorinated aromatics [1]. Because the rate constants for each successive fluorination are not widely different, producing high yields of intermediate products is difficult.

Underfluorinated material can be recycled. However, unless the goal is the perfluorocompound, overfluorinated material is a yield loss. Others have recognized this problem previously, and have attempted to develop processes for recycling overfluorinated materials. Two patents have discussed the equilibration:

$$C_6F_nCl_{6-n} = C_6F_{n+1}Cl_{5-n} + C_6F_{n-1}Cl_{7-n}$$

one from either direction [2,3]. Mahler patented a process to recycle over-fluorinated material by a thermal conproportionation reaction [2]. The conditions were extreme, and not practical. In the other direction, Nyman used a rather ineffectual AlF_3 catalyst at 700° C to promote the equilibration [3].

Olah equilibrated chloro- and bromobenzenes with $AlCl_3/H_2O$ catalysts in the liquid phase [4]. Mixed halofluorocarbons equilibrated, but difluorobenzenes did not. Dichlorobenzene isomerized intramolecularly. Dibromobenzene disproportionated and equilibrated intermolecularly. Shinoda and Yasuda found that $Pd/Cl_2/CeCl_3$ catalyzed both isomerization and disproportionation of dichlorobenzenes [5].

Chromium oxide scrambles halogens in highly halogenated compounds. It is the preferred catalyst for scrambling fluorine and chlorine on sp^2 olefinic type carbons [6]. It is also a good catalyst for scrambling halogen on sp^3 saturated carbons [7].

Selected solid Lewis acids greatly accelerate halogen scrambling among polyhaloaromatic compounds [8]. Variables such as catalyst composition, substrate, temperature and contact time all influence the course of the reaction. Severe reaction conditions or outstanding catalysts produce equilibrium information. Milder conditions or poorer catalysts give kinetic information.

RESULTS

C_6F_5X Disproportionation

Bromofluorobenzenes. Figure 1 shows the product distribution which results from passing 1 ml/hr C_6F_5Br and 5 ml/min N_2 over 5 g of Cr_2O_3 as a function of temperature. The system is essentially at the disproportionation equilibrium at 500° C. The disproportionation equilibrium is nearly statistical. Small amounts of $C_6F_4Br_3$ form, but the higher brominated products are not stable enough to quantify at these temperatures. The precision of our analysis is not good enough to establish an enthalpy for the disproportionation equilibrium.

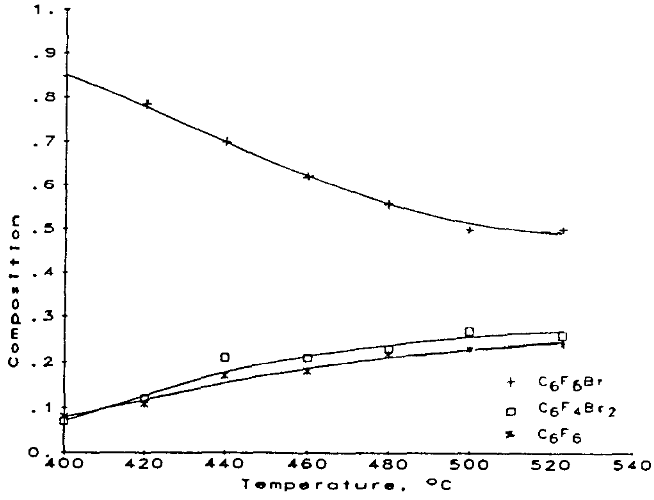

Fig.1. Product distribution

The initial $C_6F_4Br_2$ distribution is approximately 20% o, 40% m, and 40% p. As the reaction severity increases, the relative concentration of the ortho isomer decreases and the meta and para begin to approach a statistical distribution. At 520° the equilibrium distribution is approximately 11% o, 61% m, and 27% p.

Chlorofluorobenzenes. The system $C_6F_xCl_{6-x}$ has seven compositions ranging from x=0 to x=6. Counting isomers, there are 13 compounds in this equilibrium. Characterizing such a complicated equilibrium is not a trivial task.

Our FS-1265 capillary GC column could not separate all the isomers. While the column gave good separations of each group of x's, it could only separate the individual isomers for x=2. We used fluorine nmr to analyze the individual isomers.

The equilibrium composition of any disproportionation reaction, including all the isomers, is approximately statistical. Table 1 gives the equilibrium among each set of isomers of the $C_6F_nCl_{6-n}$ for n=2,3,4. The equilibria between sets with different halogen numbers are not reliable enough to calculate the free energies for the entire 13 component equilibrium.

TABLE 1

Chlorofluorobenzene Equilibrium[a] mole %

Formula	Isomers		
$C_6F_2Cl_4$	1,2 21	1,3 54	1,4 25
$C_6F_3Cl_3$	1,3,5 28	1,2,4 59	1,2,3 13
$C_6F_4Cl_2$	1,2 19	1,3 56	1,4 25

[a] Each row sums to 100%.

Iodofluorobenzenes. Iodopentafluorobenzene disproportionates in the presence of Cr_2O_3 as low as 300 °C. Adventitious protons in the system readily reduce the iodide to pentafluorobenzene. Interference by this unwanted reduction did not allow us to determine the thermodynamics of either iodopentafluorobenzene disproportionation or diiodotetrafluorobenzene equilibration.

^{19}F NMR Studies. Two groups measured the chemical shifts of all the isomers of the $C_6F_xCl_{6-x}$ [9]. A regression analysis of these shifts with respect to the number of ortho, meta and para chlorines gave a good linear fit (r^2 = 0.99, N=20) to the equation:

$$\begin{array}{llll} \text{Delta} = 163.1 & -23.3 * \#(\text{o-Cl}) & -2.2 * \#(\text{m-Cl}) & -4.9 * \#(\text{p-Cl}) \quad (1) \\ \text{Std Dev} & \pm 0.5 & \pm 0.6 & \pm 0.9 \end{array}$$

Bromochlorofluorobenzenes. To show the extent of the scrambling process we passed 1 ml/hr of a liquid composed of 2.5g 1,3,5-$C_6F_3Cl_3$ and 3ml C_6F_5Br with 10 ml N_2 over 5g of Cr_2O_3 at several temperatures. Figure 2 shows the total ion current of a GC/MS of the mixture produced at 500° C. Each well-resolved multiplet corresponds to a separate empirical formula. The earliest peak is C_6F_5Cl and the latest peaks are

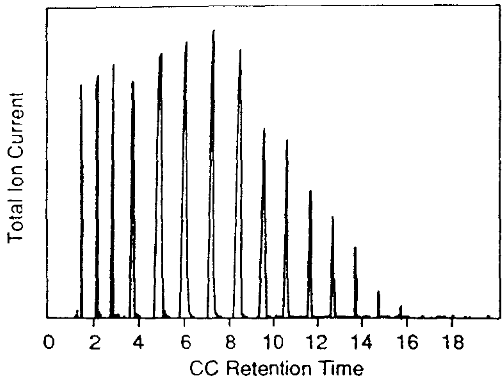

Fig.2. GC/MS of $C_6F_xCl_yBr_z$.

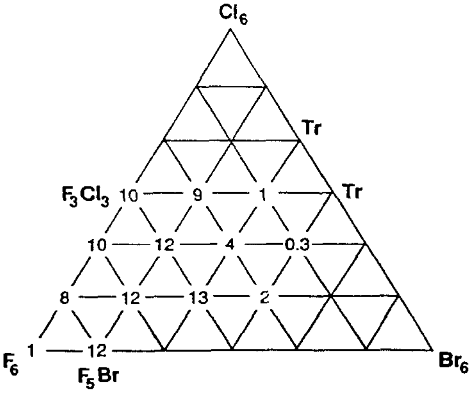

Fig.3. Composition Diagram of $C_6F_xCl_yBr_z$.

heavily brominated compounds such as $C_6Cl_3Br_3$. Many of the peaks are further resolved into the individual structural isomers.

Figure 3 shows a plot of the mole % of each composition. For a true equilibrium there should be a ring of structures around the equilibrium composition. The compounds observed should differ by at most one or two halogens from the center point. The average composition should be the same as the starting feed. This sample is not completely equilibrated as the two starting materials, C_6F_5Br and $C_6F_3Cl_3$, are still more prominent than their interior neighbors. Scrambling, however, is quite extensive.

Aromatic Structure. Other aromatic rings than phenyl can be used. C_6F_5Br was the bromine donor; F-naphthalene and F-biphenyl were the acceptors. The disproportionation chemistry of C_6F_5Br was always a check that the catalyst was active. We dissolved the acceptors in C_6F_5Br to the limits of their solubility and passed the solution over Cr_2O_3. GC/MS showed the presence of bromine substituted F-naphthalenes and F-biphenyls from the 600^o run. ^{19}F nmr showed there was no isomer selectivity.

Chlorofluoropyridines. Cr_2O_3 equilibrates pentafluoropyridine and perhalopyridines containing chlorine. Initially we studied solutions of pentachloropyridine in pentafluoropyridine. The mixtures contained only small amounts of C_5Cl_5N because its solubility in C_5F_5N is quite low.

GC/MS confirmed the presence of all the possible intermediate formulas with both Cl and F. ^{19}F nmr detected at least four out of the possible six dichlorotrifluoropyridines. There was no evidence for either 3,4,5- or 2,4,5-trifluorodichloropyridine. Exchange is most rapid **for meta to the nitrogen.** The initial products from the perhalo compounds are 2-, and 4-fluoro 2,4- and 2,6-difluoro and 2,4,6-trifluoropyridines.

Table 2 shows the product composition obtained by passing an equimolar mixture of pentafluoropyridine and 2,4,6-trifluoro-3,5-dichloropyridine over Cr_2O_3 at 520 ^oC.

3,5-Dichloro-2,4,6-trifluoropyridine conproportionates with pentafluoropyridine, to give chlorotetrafluoropyridines. The major product is 5-chloro-2,3,4,6-tetrafluoropyridine, the product from a single C-3, Cl-F exchange on both partners. Disproportionation also gives difluorotetrachloropyridines. The major isomers have replaced one of the three fluorines with chlorine. There are much smaller amounts of difluoropyridines with meta fluorines.

TABLE 2

Fluorochloropyridines[a] mole %

Formula	Isomers				
$C_5F_2Cl_3N$			2,4 3	2,6 10	
$C_5F_3Cl_2N$	2,3,6 16	2,4,6 26	2,4,5 3	2,3,5 1	2,3,4 1
$C_5F_4Cl_1N$	2,3,4,5 1		2,3,4,6 20		2,3,5,6 15
$C_5F_5Cl_0N$	5				

[a] by F-nmr.

The fluorine nmr parameters of all the chlorofluoropyridines are not in the literature. Table 3 lists the fluorine chemical shifts and splitting patterns for the perhalopyridines we measured. There are 19 pyridines with the formula $C_5F_xCl_{5-x}N$, $x>0$. There are 44 separate chemical shifts possible among these compounds. We can now assign most of these, but a few ambiguities remains.

We have not been able to distinguish the chemical shifts of 3-fluorotetrachloropyridine and 3,5-difluorotrichloropyridine. Both are relatively minor products, and both are singlets in the ^{19}F nmr. In principle, we could distinguish the two by examining the C-13 satellite spectrum. The monofluoride would show a simple doublet while the difluoride would be a doublet of doublets from the fluorine-fluorine coupling.

No signals could be assigned to either 2,4,5- or 3,4,5-trifluorodichloropyridine. Both would demand almost a complete inversion of the F-Cl substituent pattern during the halogen scrambling reaction. Their absence might be due to either kinetic or thermodynamic effects.

A regression analysis of the ^{19}F chemical shifts of the chlorofluoropyridines gave a good fit ($r^2 = 0.995$, N=35) with three **parameters:**

$$\begin{array}{llllll} \text{Delta} = 133.2 & - 19.7 * \#(\text{o-Cl}) & - 46.1 * (\text{o-N}) & + 26.3 * (\text{m-N}) & & (2) \\ \text{Std Dev} & \pm 0.6 & \pm 1.0 & \pm 1.0 & & \end{array}$$

where o-Cl is the number of ortho chlorines and x-N indicates where the fluorine being studied is relative to the nitrogen.

TABLE 3

F-19 NMR Parameters for Chlorofluoropyridines[c]

Compound	C-2[a]	C-3	C-4	C-5	C-6[a]
2-F	67.2	-	-	-	-
3-F	-	b	-	-	-
4-F	-	-	92.4	-	-
2,3-F_2	84.6	137.2 d(22.5)	-	-	-
2,4-F_2	67.9 d(16)	-	92.6 d(16)	-	-
2,5-F_2	68.9	-	-	119.5 d(26)	-
2,6-F_2	68.7	-	-	-	68.7
3,4-F_2	-	139.6 d(21)	115.5	-	-
3,5-F_2	-	b	-	b	-
2,3,4-F_3	85.5	160.0	112.9 t(19)	-	-
2,3,5-F_3	82.4	141.5 dd(19,25)	-	115.6 dd(12,19)	-
2,3,6-F_3	87.1	140.8 dd(21,26)	-	-	71.0
2,4,6-F_3	69.6 d(13)	-	93.3 t(13)	-	69.6 d(13)
2,3,4,5-F_4	83.5	158.0	135.3	138.9	-
2,3,4,6-F_4	85.1	162.9 q(18)	113.3 d(10),t(18)	-	71.8
2,3,5,6-F_4	88.7	141.9	-	141.9	88.7
2,3,4,5,6-F_5	86.6	160.9	132.8	160.9	86.6

[a] These resonances are broad because they interact with the N-14 quadrupole.

[b] Either 116.5 or 117.5

[c] In ppm, + UPFIELD from $CFCl_3$

The other parameters are not significant. The standard error of the fit is 2.3 ppm over a range of 100 ppm.

Substituents Tolerated on the Aromatic Ring. Chlorine and bromine catalytically exchange in pentahalobenzenes with some non-halogen substituents. The substituent must be stable to the still rather severe reaction conditions. Cyano, CF_3 and H are suitable. Nitro, and carbonyls, are not.

Feeding either $C_6F_5CF_3$, C_6F_5CN, or C_6F_5H, and C_6F_5Br exchanges bromine for fluorine in the three substrates. There was no significant exchange of either H, CF_3 or CN to give compounds with two of these functionalities. There was no significant isomer preference to the bromine incorporation.

Perhalogenated aromatics scramble freely, and one hydrogen is tolerated. We then asked could there be more than one hydrogen. 1,2,3,5-$C_6H_2Cl_4$ and C_6F_6 do scramble to give some C_6Cl_4FH and $C_6Cl_4F_2$, but the reaction is very slow. Cr_2O_3 did not catalyze scrambling between C_6F_5H and 1,2,4-$C_6H_3Cl_3$ up to 600°. No products containing H, Cl and F form from passing $C_6F_3Cl_3$ and $C_6H_3Cl_3$ over Cr_2O_3. For reasonable results, no more than one hydrogen should be present on the aromatic ring.

Catalyst Studies. Catalyst scouting was done with C_6F_5Br as substrate. The two major products are C_6F_6 and the three isomers of $C_6F_4Br_2$. The reaction also produces small amounts of the three isomers of $C_6F_3Br_3$.

At 600° C in the contact time used for our scouting work we saw no reaction with Harshaw AL-1101, a commercial AlF_3. A material which gives ANY conversion to products below 600° C is better than AlF_3. A large number of solid Lewis acids function as catalysts [8]. Chromium oxide is uniquely active.

One factor may be the thermal stability of the chromium halides. For many other elements, one or both of the halides are too volatile to function in this chemistry. For example molybdenum fluoride boils at 35° C. Titanium tetrachloride boils at 136° C. Although the oxides of metals such as these exhibit initial activity, those which have volatile or even low melting halides have short lives as disproportionation catalysts. Both $CrCl_3$ and CrF_3 are non-volatile.

At higher temperatures and longer contact times we observed more of the heavy halogens and less fluorine in the aromatics in the gas phase. The missing fluorine is taken up by the catalyst as determined by elemental analysis. We have not run the reaction long enough to determine if there is a steady state. This halogen transfer might continue until the entire oxide catalyst becomes halogenated. Pure CrF_3 is less active than surface halogenated Cr_2O_3.

Bromine plus Hexafluorobenzene. Although not strictly a transhalogenation, the results of reacting bromine with C_6F_6 in the presence of Cr_2O_3 are relevant to this paper. The operative reaction appears to be equation 3.

$$C_6F_6 + Br_2 \longrightarrow C_6Br_6 + C_6F_{10} \qquad (3)$$

GC/MS also detected a small amount of $C_6F_{11}Br$. A possible reaction sequence might involve addition of bromine to the aromatic ring followed by catalyzed halogen scrambling to the observed products. Fluorine prefers to bond to sp^3 rather than sp^2 carbon.

EXPERIMENTAL

General Remarks. ^{19}F NMR spectra in $CDCl_3$ were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz. Chromium oxide, surface area 42 m^2/g particle size 10-20 mesh, was prepared by the pyrolysis of ammonium dichromate.

Liquid Phase Process. A mixture of 1g C_6FCl_5 and 0.2g Cr_2O_3 was refluxed in a round-bottom flask with an air condenser. We had to periodically melt a sublimate to recontact it with the catalyst. A GC analysis of the product showed 5 area% $C_6F_2Cl_4$, 83% C_6FCl_5, and 10% C_6Cl_6.

Vapor Phase Process. Liquids were fed using a Sage syringe pump to catalyst in a 3/4" x 5" Vycor^r reactor heated by a split tube furnace. A typical catalyst charge was 5g. Typical liquid flow rates were 0.5 to 2 ml/hr liquid with 5-20 ml/min N_2 as carrier gas. The reaction effluent was passed through heated lines to a Valco^r 10-port sample valve in a Varian-6000 GC equipped with a flame ionization detector. A 30m capillary column coated with FS-1265, a CF_3CH_2O-silicone derivative, separated most of the mixtures by empirical formula. The column only rarely separated individual isomers. Selected samples were condensed at -78^o C and products submitted for GC/MS or ^{19}F nmr analysis.

CONCLUSION

Cr_2O_3 catalyses halogen scrambling in polyhaloaromatic compounds. All four halogens (F, Cl, Br, and I) exchange. The chemistry works for benzenes, pyridines, and naphthalenes as the aromatic ring. Tolerated substituents which do not themselves scramble include R_f, CN, and a single H.

ACKNOWLEDGEMENT

D. C. Roe ran the 2-dimensional fluorine nmr spectra of th polyhalopyridines.

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