REACTION OF PEROXYDISULFURYL DIFLUORIDE WITH FLUOROALKYL HALIDES

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The reactions of peroxydisulfuryl difluoride $(FSO_2O)_2$ with fluoroalkyl halides have not been studied extensively. $(FSO_2O)_2$ reacts with perfluoroalkyl iodides at $\leq -50°C$ to give trivalent iodine derivatives, $R_FI(OSO_2F_2)$, which, depending on the type of perfluoro group, may be stable at 20°C or decompose to the corresponding perfluoroalkyl fluorosulfates and $IOSO_2F$ [1-4]. In the case of $CF_2ClCFCl_2$ (Freon-113), $(FSO_2O)_2$ is much less reactive toward fluoroalkyl chlorides than chlorine and bromine fluorosulfates. $(FSO_2O)_2$ does not react with Freon-113 even upon prolonged heating at 150°C. This reaction begins at ~150°C upon catalysis by HSO_3F [5]. In the presence of HSO_3F/SbF_5, we find exothermal substitution of the $CFCl_2$ group chlorine atom by a fluorosulfate group [6].

In the present work, $(FSO_2O)_2$ was found to be less active in reactions with perfluoroalkyl bromides than chlorine and bromine fluorosulfates. Thus, $(FSO_2O)_2$ does not react with 1,2-dibromotetrafluoroethane (DBE) and 1,4-dibromooctafluorofluorobutane (DBB) at the boiling points of the reaction mixtures. An exothermal reaction of $(FSO_2O)_2$ with DBE and DBB begins at ~ 50-60°C upon the addition of ~5 mole % bromine. This results from the formation of bromine tris(fluorosulfate), $Br(OSO_2F)_3$ from Br_2 and $(FSO_2O)_2$; $Br(OSO_2F)_3$ is the most active of the halofluorosulfates in the substitution of halogens by the FSO_2O group in fluoroalkyl halides [7] and is regenerated from $(FSO_2O)_2$ and $BrOSO_2F$ which is generated during the course of the reaction. The fluorosulfation of DBE and DBB in this case may be represented by the following scheme:

$$Br_2 + (FSO_2O)_2 \rightarrow Br(OSO_2F)_3 \leftarrow (FSO_2O)_2 + BrOSO_2F$$

$$Br(OSO_2F)_3 + Br(CF_2)_nBr \rightarrow Br(CF_2)_nOSO_2F + 2BrOSO_2F$$

$$BrOSO_2F + Br(CF_2)_nBr \rightarrow \underset{(I),\ (II)}{Br(CF_2)_nOSO_2F} + Br_2$$

$$n = 2\ (I),\ 4\ (II).$$

Relatively prolonged heating of the reaction mixture at 70-80°C is required to obtain ω-bromoperfluoroalkyl fluorosulfates (I) and (II) with rather high yields in the case of initial $(FSO_2O)_2{:}Br(CF_2)_nBr$ mole ratio equal to 1:2 (i.e., in order to effect fluorosulfation of $BrOSO_2F$ formed). This is in accord with our previous data on the reaction of $BrOSO_2F$ with DBE [8]. In this case, the products of the substitution of two bromine atoms are formed in slight amounts. We should note that this reaction requires the use of freshly prepared reagents and conditions excluding moisture. Otherwise, the formation of fluorosulfonic acid may be formed, which, as we have established, has a significant effect on the reaction of $(FSO_2O)_2$ with DBE and DBB. Thus, an exothermal reaction between $(FSO_2O)_2$ and the bromides studied begins at 30-35°C upon HSO_3F catalysis. Under these conditions, substitution of a bromine atom with the liberation of $BrOSO_2F$ occurs at the onset upon the action of $(FSO_2O)_2$.

$$(FSO_2O)_2 + Br(CF_2)_nBr \xrightarrow{HSO_3F(cat),\ 30-35°} Br(CF_2)_nOSO_2F + BrOSO_2F$$

$Br(OSO_3F)_3$ and $BrOSO_2F$ act as fluorosulfating agents in the subsequent steps. The reactivity of these species in the presence of HSO_3F is sharply enhanced. This process should be used for the synthesis of the products of both bromine atoms in DBE and DBB by FSO_2O groups as described by the overall scheme:

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$$(FSO_2O)_2 + Br(CF_2)_nBr \xrightarrow{HSO_3F(cat)} \underset{(III),\,(IV)}{FSO_2O(CF_2)_nOSO_2F} + Br_2$$

$n = 2$ (III), 4 (IV).

Heating at 50-60°C is required to obtain high yields of bis(fluorosulfates) (III) and (IV).

The effect of strongly acidic additives on the reactivity of $(FSO_2O)_2$ and halofluorosulfates [9] is apparently related to the increase in the oxidative capacity. The superacid HSO_3F/SbF_5 has the greatest effect in this case [6-9]. However, $(FSO_2O)_2$, in contrast to chlorine and bromine fluorosulfates, does not replace the chlorine atom in the CF_2Cl group in 2-trifluoromethyl-2,3-dichloropentafluoropropane (TDP) and 1,2-dichlorohexafluoropropane (DCP) in the presence of HSO_3F/SbF_5. The introduction of slight amounts of $BrOSO_2F$ or Br_2 to the reaction mixture, which is equivalent to the addition of $Br(OSO_2F)_3$, was also not successful. Thus, reaction between the reagents was not noted upon heating a mixture of TDP, $(FSO_2O)_2$, HSO_3F/SbF_5, and $Br(OSO_2F)_3$ at 65-70°C for 2-4 h. This failure indicates that $(FSO_2O)_2$ in the presence of HSO_3F/SbF_5 somewhat inhibits the reactivity of $Br(OSO_2F)_3$, which, in the absence of $(FSO_2O)_2$, reacts vigorously under these conditions with TDP with the formation of β-chlorooctafluoroisobutyl fluorosulfate (V), $ClOSO_2F$, and $BrOSO_2F$ [7]. On the other hand, the addition of ~5-8 mole % $ClOSO_2F$ or Cl_2 to the reaction mixture provides for the substitution of chlorine in TDP and DCP in an exothermal reaction and the formation of the corresponding fluoroalkyl fluorosulfates (V) and (VI) in high yields.

$$(FSO_2O)_2 + RCF_2Cl \xrightarrow[-Cl_2]{HSO_3F/SbF_5,\ ClOSO_2F(\text{or } Cl_2)\ (cat)} \underset{(V),\,(VI)}{RCF_2OSO_2F}$$

$R = (CF_3)_2CCl$ (V), CF_3CFCl (VI).

In this case, $ClOSO_2F$ undoubtedly acts as the fluorosulfating agent. This species is readily formed from Cl_2 and $(FSO_2O)_2$ in the presence of HSO_3F/SbF_5 [10].

Thus, the replacement of the chlorine or bromine atoms in fluoroalkyl chlorides or bromides by an FSO_2O group by the action of $(FSO_2O)_2$ requires conditions for the generation of chlorine or bromine fluorosulfate *in situ* from $(FSO_2O)_2$; these fluorosulfates act as fluorosulfating reagents in this reaction.

EXPERIMENTAL

4-Bromooctafluorobutyl Fluorosulfate (II). A sample of 0.8 g (0.005 mole) bromine was added to a mixture of 80 g (0.222 mole) 1,4-dibromooctafluorobutane and 22 g (0.111 mole) peroxydisulfuryl difluoride. The reaction mass was heated with stirring at 50-60°C until the onset of an exothermal reaction. Stirring was continued, maintaining the temperature not above 60°C until heat is no longer released. Then, the mixture was heated for an additional 4.5 h at 70-80°C. The major portion of unreacted bromine was distilled out of the reaction mixture. The residue was washed with 5% aq. hyposulfite (until it was decolorized) and water, dried over $MgSO_4$, and distilled to give 65.4 g (78%) 4-bromooctafluorobutyl fluorosulfate (II), bp 116-118°C, n_D^{20} 1.3293, d_4^{20} 1.979. Found, %: C 12.41; Br 20.73; F 45.50; S 8.37. $C_4BrF_9O_3S$. Calculated, %: C 12.66; Br 21.11; F 45.12; S 8.44. We also isolated 4.1 g (5%) 1,4-bis(fluorosulfonyloxy)octafluorobutane (IV), bp 137-318°C, d_4^{20} 1.787, n_D^{20} 1.3105 [11].

Under analogous conditions, a 2:1 mixture of 1,2-dibromotetrafluoroethane and peroxydisulfuryl difluoride in the presence of ~5 mole % bromine gave 2-bromotetrafluoroethyl fluorosulfate (I) in 75% yield, bp 73-75°C, d_4^{20} 1.901, n_D^{20} 1.3237 [8] and 1,2-bis(fluorosulfonyloxy)tetrafluoroethane (III) in 4% yield, bp 101-102°C, d_4^{20} 1.790, n_D^{20} 1.3489 [8].

1,4-Bis(fluorosulfonyloxy)octafluorobutane (IV). A sample of 40 g (0.111 mole) 1,4-dibromooctafluorobutane was added dropwise with stirring to 22 g (0.111 mole) peroxydisulfuryl difluoride containing 1 ml HSO_3F at 30-40°C. Stirring was continued at 40°C for an additional 2 h. The reaction mixture was treated as indicated above to give 37.7 g (85%) 1,4-bis(fluorosulfonyloxy)octafluorobutane (IV), bp 137-138°C, d_4^{20} 1.787, n_D^{20} 1.3105 [11].

Under analogous conditions, a 1:1 mixture of 1,2-dibromotetrafluoroethane and peroxydisulfuryl difluoride in the presence of HSO_3F gave 1,2-bis(fluorosulfonyloxy)tetrafluoroethane (III) in 87% yield, bp 101-102°C, d_4^{20} 1.790, n_D^{20} 1.3489 [8].

β-Chlorooctafluoroisobutyl Fluorosulfate (V). A sample of 1.7 g (0.024 mole) chlorine was added to a mixture of 57.9 g (0.3 mole) peroxydisulfuryl difluoride, 6 g SbF_5, and 16 g HSO_3F. Then, 162.6 g (0.6 mole) 2-trifluoromethyl-2,3-dichloropentafluoropropane was added dropwise with stirring at 25-30°C. Stirring was continued for an additional 1 h at 30°C and 1 h at 60-70°C and distilled to give 159.6 g (80%) β-chlorooctafluoroisobutyl fluorosulfate (V), bp 97-99°C, d_4^{20} 1.762, n_D^{20} 1.3104 [8].

Under analogous conditions, 1,2-dichlorohexafluoropropane and peroxydisulfuryl difluoride containing 5 mole % chlorine fluorosulfate in the presence of HSO_3F/SbF_5 gave β-chlorohexfluoropropyl fluorosulfate (VI) in 79% yield, bp 76°C, d_4^{20} 1.701, n_D^{20} 1.3071 [3].

CONCLUSIONS

The replacement of bromine in perfluoroalkyl bromides by an FSO_2O group by the action of $(FSO_2O)_2$ occurs upon catalysis by Br_2 or HSO_3F, while the fluorosulfation of perfluoroalkyl chlorides by peroxydisulfuryl difluoride is achieved in the presence of superacid HSO_3F/SbF_5 and catalytic amounts of $ClOSO_2F$ or Cl_2.

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