Reactions of the Bistrifluoromethylnitroxide Radical with Halides

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THE highly electronegative bistrifluoromethylnitroxide radical, $(CF_3)_2NO\bullet$, resembles a halogen in many of its reactions. It will, for example, combine directly with lead,[1] mercury,[2] selenium, and tellurium[3] to form the corresponding bistrifluoromethylnitroxides. We have recently observed that it can liberate bromine or iodine at or below room temperature from certain iodides or bromides and, in a few cases, chlorine from chlorides. The latter reaction is catalysed by the presence of iodine.

This type of reaction was first found in a study of the reaction of the radical with SiH_3Br, SiH_2I_2, and GeH_3I. Hydrogen was removed as bistrifluoromethylhydroxylamine, $(CF_3)_2NOH$, all of the halogen was liberated as such and the compounds $[(CF_3)_2NO]_4Si$ and $[(CF_3)_2NO]_4Ge$ were recovered almost quantitatively. A similar quantitative displacement of halogen was observed with BBr_3, $AsBr_3$, AsI_3, $BiBr_3$, BiI_3, and BiOI. Tris(bistrifluoromethylnitroxy)bismuthine, $[(CF_3)_2NO]_3Bi$, may also be prepared from the radical and the element at room temperature. Sodium iodide was converted quantitatively into sodium bistrifluoromethylnitroxide, which in turn was converted into sodium chloride by reaction at 20° with HCl, producing bistrifluoromethylhydroxylamine. Sodium bromide has also been found to react with the nitroxide free-radical. Caesium iodide on the other hand took up and retained two moles of radical per mole of CsI and formed a light-sensitive buff coloured solid $CsI[ON(CF_3)_2]_2$ which is analogous to the polyhalide $CsICl_2$. Cobalt iodide was converted by radical into the compound $Co[ON(CF_3)_2]_2$. This was decomposed at 80° to a complex mixture of products. Bistrifluoromethylhydroxylamine was also liberated quantitatively from the cobalt compound by reaction with gaseous HCl.

The gaseous bistrifluoromethylnitroxide radical reacted rapidly and quantitatively with gaseous HBr or HI at temperatures appreciably less than 20°, the products being the hydroxylamine and free halogen. Reaction with HCl under comparable conditions was very slow, *e.g.* 10% conversion into the hydroxylamine in 13 days at 20°. In presence of 5 mole % of free iodine, based on the HCl taken, reaction was complete in 2 hr. Iodine was converted into ICl_3, free chlorine was present, and all of the hydrogen appeared as $(CF_3)_2NOH$. Reaction of BCl_3 with bistrifluoromethylnitroxide was slow, but was again greatly accelerated by the presence of iodine. Arsenic trichloride, however, did not react with the radical at temperatures up to 100° but, in presence of sufficient iodine to convert all of the chlorine into ICl, was converted rapidly into $[(CF_3)_2NO]_2AsCl$. The fully substituted compound, tris(bistrifluoromethylnitroxy)arsine, is produced when arsenic trichloride reacts with mercury(II) bistrifluoromethylnitroxide.[2]

The influence of stoicheiometric amounts of iodine in promoting the reaction of the radical with these chlorides may be due to its combination with free chlorine, which is known to react with $[(CF_3)_2NO]_3As$ to re-form $AsCl_3$. We have obtained no evidence of compound formation between iodine and the bistrifluoromethylnitroxide radical and the specific conductivity of the latter in the liquid state ($< 10^{-7}$ ohm^{-1}, cm.$^{-1}$) is not appreciably increased by the addition of iodine. It is possible that an unstable active intermediate such as $ICl[ON(CF_3)_2]_2$ could account for the catalytic effect reported above. The instability of such an intermediate is supported by the fact that there is no retention of the nitroxide free-radical by ICl at room temperature or as low as −70°.

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