Kirk-Othmer Encyclopedia of Chemical Technology.

BROMOTRIFLUOROETHYLENE

Bromotrifluoroethylene is a valuable reagent for the synthesis of trifluorovinylic compounds by means of its intermediate organometallic compounds.

1. Physical Properties

The monomer, bromotrifluoroethylene [598-73-2], $CF_2{=}CFBr$, is a colorless gas; bp −3.0°C at 101 kPa (754 mm Hg); 58°C at 790 kPa (100 psig); and $d^{25}{}_4$ 1.86 g/cm^3. Since it is spontaneously flammable in air, its odor is that of its oxidation products, mixed carbonyl halides. The olefin can be distilled, but it polymerizes on standing at ambient temperature unless an inhibitor such as 0.1% tributylamine is added. If desired, the inhibitor can be readily removed by passing the gas through silica gel. Higher temperatures or uv light increase the polymerization rate. The nmr (1, 2), ir (3), uv (4), and photoelectron spectra (5) of the monomer have been reported, and some thermochemical data have been calculated for it (3). Its dipole moment has been determined to be 2.54×10^{-30} C·m (0.76 D) (6).

2. Chemical Properties

Many reactions of bromotrifluoroethylene have been studied. Under basic conditions it adds alcohols such as methanol (7, 8) or ethanol (8, 9), forming ethers with the general formula $ROCF_2CFBrH$. Similarly, diethylamine adds to it giving $(C_2H_5)_2NCF_2CFBrH$ (10). This addition is faster than diethylamine additions to tetrafluoroethylene or chlorotrifluoroethylene. Vapor-phase photochemical bromination of bromotrifluoroethylene gives the expected adduct, $CF_2BrCFBr_2$ (11). On the other hand, photochemical chlorination results in only 60% of the expected adduct and 40% scrambled bromo and chloro products. Hydrogenation of the double bond can be accomplished either catalytically (12) or with sodium borohydride (13). The former method also gives some trifluoroethylene and the latter method gives only a 37% yield of the pure product, $CF_2HCFBrH$. Other reagents that add across the double bond include S_2Cl_2, to give mainly a disulfide (14), and aqueous sodium nitrite (15).

Another class of reactions that bromotrifluoroethylene undergoes is cycloaddition with acetylenes (16) or olefins (17). When heated, the pure monomer, in addition to polymerizing, dimerizes to *cis*- and *trans*-1,2,-dibromohexafluorocyclobutane, which can be debrominated with zinc to perfluorocyclobutene [697-11-0] (18). Bromotrifluoroethylene is a valuable reagent for the synthesis of trifluorovinylic compounds by means of its intermediate organometallics. Trifluorovinylzinc (19) and trifluoromagnesium bromides (20, 21) may be prepared directly using the metals, whereas trifluorovinyllithium [683-78-3] results from the metathesis metal–bromine exchange (22). The lithium and magnesium derivatives are thermally unstable but readily convert aldehydes, ketones, and carbon dioxide to alcohols (22, 23) and trifluoroacrylic acid [433-68-1] (20). The zinc derivative transforms iodo- or bromobenzenes to α,β,β-trifluorostyrenes in the presence of zero valent palladium complexes (24) and participates in a variety of alkylation, coupling, and acylation reactions upon the addition of cuprous salts (25).

3. Manufacture

Although bromotrifluoroethylene was first prepared (9) by the dehydrobromination of 1,2-dibromo-1,1,2-trifluoroethane [354-04-1], it is more conveniently prepared from chlorotrifluoroethylene [79-38-9] by the following high yield steps (26):

$$CF_2{=}CFCl + HBr \longrightarrow CF_2BrCFClH \xrightarrow{Zn} CF_2{=}CHF + ZnBrCl$$

$$CF_2{=}HF + Br_2 \longrightarrow CF_2BrCHFBr \xrightarrow{KOH} CF_2{=}CFBr + KBr + H_2O$$

Bromotrifluoroethylene is manufactured and sold in commercial quantities with a purity of 99.9% by the Halocarbon Products Corp. for about $100/kg as of 1992.

4. Polymers

The olefin can be polymerized in trichlorofluoromethane solution at $5^\circ C$ for 7 days with a halogenated acetyl peroxide such as 0.037% trichloroacetyl peroxide as the initiator (27). Alternatively, it may be polymerized in an aqueous suspension with 2 parts by weight distilled water, 0.01 part ammonium persulfate, 0.004 part sodium bisulfite, and 0.001 part hydrated ferrous sulfate present for each part of the monomer. Mixing for 24.5 h at 20°C gives a 52% conversion of the monomer to the homopolymer (27). Prepared either way, the homopolymer [55157-25-0] is a white powder soluble in acetone and useful as a hard, chemically resistant coating for metal or fabric surfaces. The addition of small amounts of chain-transfer agents such as chloroform, carbon tetrachloride, bromotrichloromethane, and in particular, 0.01 to 0.3% 1-dodecanethiol to the polymerization mixture gives a lower molecular weight homopolymer that is softer and more soluble. Copolymers of bromotrifluoroethylene with many other monomers such as chlorotrifluoroethylene (28), tetrafluoroethylene (29), or trifluoronitrosomethane (30) have been reported. Neither the homopolymer nor the copolymers have any commercial utility.

4.1. Telomers.

Bromotrifluoroethylene telomers have been prepared using chain-transfer agents such as CF_3SSCF_3 (31), C_2F_5I (32), CBr_4 (32), or CBr_3F (33). For example, when the olefin is slowly added to tribromofluoromethane under light from sunlamps, a liquid is obtained which, after saturation and distillation, has a viscosity of 510 $mm^2/s(=cSt)$ and a density of 2.65 g/cm^3 at 58.3°C. These and other bromotrifluoroethylene telomers are useful as flotation agents and damping fluids for gyroscopes and accelerometers in inertial guidance systems. These telomers are noncrystalline up to a higher degree of polymerization than those of chlorotrifluoroethylene, allowing the preparation of liquids of greater viscosity. The higher densities of the bromine-containing oils permit further miniaturization of the instruments floating in them. For these reasons, these oils complement their less expensive chloro analogues in this application. Commercially available bromotrifluoroethylene telomers have densities of 2.14–2.65 g/cm^3 and viscosities of $2 - 4000\ mm^2/s(=cSt)$. These fluids are expensive but are made in small volume for the aerospace industry.

5. Toxicity

Rats exposed to 500 ppm of bromotrifluoroethylene died following a 4-h exposure. Since the monomer decomposes in air, the level of exposure to it was actually lower. The effects in rats of repeated exposure over a two-week period have been studied. At 50 ppm, the animals lost weight and renal damage was noted although the effect was reversible. Very mild testicular damage was seen at 50 but not 10 ppm. The amount of urinary fluoride excreted suggested that extensive metabolism was occurring (34).

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