ization of the hydrocarbon framework as T^{2-} is converted into $T^{\cdot -}$ is responsible for the slowness of those reactions.

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Preparation of an Alkyl Perbromate[1]

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Abstract: Silver perbromate was prepared by the reaction of dilute aqueous perbromic acid with silver oxide. Anhydrous silver perbromate suspended in carbon tetrachloride, cyclohexane, or 1,1,2-trichlorotrifluoroethane at −20° reacted with isopropyl bromide to give a 95% yield of isopropyl perbromate. At room temperature, isopropyl perbromate decomposed to give acetone in high yield.

Perbromic acid was prepared in 1968[2] after numerous unsuccessful synthesis attempts and theoretical rationalizations for its nonexistence were reported.[3] The chemistry of this interesting acid remains virtually unexplored, other than its oxidizing properties toward inorganic reagents[4] and the preparation of its alkali metal[4] and ammonium[5] salts. Reconciling the sluggish chemical oxidizing properties of perbromates, their electrode potential[6] (1.74 V compared to 1.23 V for perchlorate) and the difficulty of their preparation have been a subject of speculation.[3] The preparation of an ester of perbromic acid was of interest for the possibility that its properties might shed light on this problem, as well as from the standpoint of a new organic functional group.

One method that would appear attractive for the synthesis of alkyl perbromates is the reaction of dibromine heptoxide with alcohols, since the corresponding reaction of dichlorine heptoxide is a convenient source of alkyl perchlorates.[7] Dibromine heptoxide, however, has not been prepared, and attempts to dehydrate aqueous perbromic acid at room temperature resulted in autocatalytic decomposition after the dihydrate stage.[4] Another versatile route to alkyl perchlorates is the reaction of silver perchlorate with alkyl halides.[8,9] Application of this method to perbromates requires silver perbromate, which also has not been reported. Indeed, silver ion was reported to catalyze the decomposition of 6 *M* perbromic acid[4] at 100°.

Dilute aqueous perbromic acid is much more stable than the concentrated acid, and alkali salts of perbromic acid are relatively stable, both as solutions and as neat materials. The approach was therefore taken to prepare silver perbromate in dilute aqueous solution, followed by removal of water. A 0.5 *M* solution of perbromic acid was prepared by the procedure of Appelman, using elemental fluorine to oxidize bromate.[10] The perbromic acid was stirred at ambient temperature with the theoretical amount of silver oxide. The bulk of water was removed under vacuum, and the concentrate was dried by azeotroping with benzene. The product, which was soluble in benzene, was precipitated by the addition of hexane. The isolated yield was 88%.

$$Ag_2O + 2HBrO_4 \longrightarrow 2AgBrO_4 + H_2O$$

Silver perbromate was identified by analysis for silver, using sodium chloride. It reacted with saturated aqueous hydrobromic acid to give the theoretical amount of bromine, determined iodometrically, using the conditions reported for the analysis of perbromic acid.[10] The appearance and solubility properties of silver perbromate are similar to those of anhydrous silver perchlorate; it is a white hygroscopic solid, soluble in benzene and insoluble in saturated hydrocarbons. The material was unchanged in several months at ambient temperature.

Attempts were made to prepare alkyl perbromates by treating alkyl iodides with suspensions of silver perbromate in carbon tetrachloride at 0°. An immediate reaction took place, producing elemental iodine. No simple organic compounds were detected by nmr. When a solution of isopropyl perbromate in carbon tetrachloride, described below, was treated with ethyl iodide at −20°, iodine was also liberated rapidly. Thus, the oxidizing properties of alkyl perbromates are incompatible with their preparation from alkyl iodides and silver perbromate.

To avoid this oxidative side reaction, bromine was used as a leaving group. Simple primary alkyl bromides were not sufficiently reactive with silver perbromate to yield a product. Isopropyl bromide, however, was consumed completely within 15 min by an equivalent amount of silver perbromate suspended in carbon tetrachloride at −20°. The product, isopropyl perbromate, was formed in 95% yield, determined by nmr using a quantitative internal standard. The only other product detected was acetone (1%). In the same way solutions of isopropyl perbromate in cyclohexane and 1,1,2-trichlorotrifluoroethane were prepared.

$$(CH_3)_2CHBr + AgBrO_4 \longrightarrow (CH_3)_2CHOBrO_3 + AgBr$$

The structure assignment of isopropyl perbromate is based on its method of formation in high yield, its spectral properties and its decomposition product. The nmr spectrum of isopropyl perbromate in carbon tetrachloride consists of a septet at δ 5.17 for the methine and a doublet at δ 1.52 for the methyl. These chemical shift values indicate an isopropyl group with a strongly electron-withdrawing substituent. The values are very close to those of isopropyl perchlorate,[7] δ 5.10 for the methine and δ 1.58 for the methyl. The ir spectrum, detailed in the Experimental Section, also supports the structure assignment. A very strong band at 790 cm^{-1} (in cyclohexane) is noteworthy, comparable to the reported band at 798 cm^{-1} for perbromic acid and its salts.[4]

Solutions of isopropyl perbromate showed no decomposition within several hours at −20°. At room temperature the compound decomposed with a half-life of about 30 min to give acetone, obtained in 90% yield after 24 hr. A similar reaction was not observed with isopropyl perchlorate, even on prolonged storage.

$$(CH_3)_2CHOBrO_3 \longrightarrow (CH_3)_2CO + HBrO_3$$

This reaction suggests that perbromate is intrinsically a considerably stronger oxidizing agent than perchlorate. The result is consistent with the assumption of a high activation barrier for reduction of perbromate used to explain their inertness.[3a] This barrier is lowered because of the intramolecular nature of the oxidation-reduction reaction leading to the formation of acetone from isopropyl perbromate.

Experimental Section

General Procedure. Although no explosions occurred in the course of this work, hazards are unknown and precautions are advised. Adequate safety shields were used, and tongs were used for manipulations in gram-scale reactions. Nmr spectra were recorded by means of a Varian T-60 spectrometer and ir spectra, by means of a Perkin-Elmer 700 spectrophotometer.

Silver Perbromate. Silver oxide (5.80 g, 0.025 mol) was added in portions, with stirring, to 100 ml of 0.5 *M* perbromic acid.[10] The mixture was stirred for 2 hr at ambient temperature and was then filtered. The bulk of water was removed from the filtrate under vacuum, and 100 ml of benzene was added. The remaining water was removed by azeotropic distillation using a Dean–Stark trap. The resulting benzene solution was filtered hot. When the solution was cooled to room temperature, 100 ml of hexane was added. The solvent was decanted from the precipitated salt, and the salt was dried briefly at 25° (0.05 mm) and was then heated with a 70° bath at 0.05 mm for 6 hr to remove adsorbed solvent. The product, 11.1 g (88%), was a white, hygroscopic, crystalline solid.

Silver perbromate was treated with hydrobromic acid in a modification of the reported analytical procedure for perbromic acid.[10] Saturated aqueous hydrobromic acid (4 ml) at −10° was added to a cooled solution of 0.1 g of silver perbromate in 0.2 ml of water. The mixture was allowed to stand for 30 min at ambient temperature. A solution (80 ml) of sodium dihydrogen phosphate (11 g) and potassium iodide (2.5 g) was added, and the liberated iodine was titrated with thiosulfate: iodometric equivalent weight, 31.84 (calcd, 31.47).

Anal.[11] Calcd for $AgBrO_4$: Ag, 42.84. Found: 43.16.

Isopropyl Perbromate. A solution of 0.123 g (1.0 mmol) of isopropyl bromide in 1 ml of carbon tetrachloride was added dropwise, with stirring, to a suspension of 0.252 g (1.0 mmol) of silver perbromate in 4 ml of carbon tetrachloride, maintained at −20° by means of a carbon tetrachloride–Dry Ice slush bath. The reaction mixture was kept at −20° for 15 min. The silver bromide was removed by filtration, giving a pale yellow solution. The same procedure was used to prepare solutions in the solvents cyclohexane and 1,2,2-trichlorotrifluoroethane: nmr (CCl_4) δ 5.17 (septet, 1 H, J = 6 Hz, $CHOBrO_3$) and 1.52 ppm (d, 6 H, J = 6 Hz, CH_3); ir (CCl_4) 3010 (m), 1460 (m), 1390 (m), 1190 (w), 1150 (m), 1100 (s), 945 (vs), 900 (m), and 860 cm^{-1} (m); ir (cyclohexane) 790 cm^{-1} (vs). The yield of isopropyl perbromate was 95%, determined by nmr integration using chlorobenzene as a quantitative internal standard. The only impurity detected was 1% of acetone. The decomposition of isopropyl perbromate solutions was monitored similarly by nmr. The solutions showed no decomposition within several hours at −20°. At ambient temperature, the compound decomposed with a half-life of about 30 min to give acetone as the only product detectable by nmr. The yield of acetone was 90% in 24 hr. The solution became red-orange in color.

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