THE SYNTHESIS OF ^{18}O-ENRICHED KO_2

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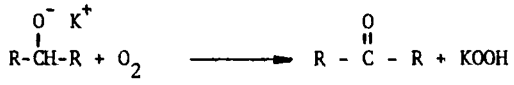
Recently, the use of superoxide salts has gained an acute interest in organic and enzymatic chemistry as a well defined source of superoxide radical anion. Studies of the chemistry of this species performed in our laboratory necessitated synthesis of an ^{18}oxygen-labeled salt. The most common, and one of the few superoxide salts which can be obtained in a pure state is KO_2. Incorporation of oxygen-18 into KO_2 by the usual methods of preparation such as atomizing molten potassium with air (1), oxidation of potassium in liquid ammonia (2,3), or burning of potassium metal in incompletely dried oxygen (4) are inconvenient.

The synthetic route employed by us was based on the reaction of oxidation of alkoxides to carbonyl compounds by molecular oxygen (5,6,7,8).



$$\overset{O^- K^+}{\overset{|}{R\text{-}CH\text{-}R}} + O_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - R + KOOH$$

$$KOOH \rightarrow \rightarrow KO_2$$

Specifically the oxidation of benzhydrol in the presence of potassium t-butoxide in benzene as described by A.Le Berre (6) was found to give the best results.

Benzhydrole (puriss, Fluka AG) mp 67°C was dried under vacuum before use. t-BuOK prepared by reaction of potassium with t-butyl alcohol was dried at 0.01 mmHg at 110°C till the complete removal of solvated t-butyl alcohol. Benzene was distilled over Na before use.

In a round-bottom flask (50 ml) provided with a magnetic stirrer, 1.15 gr benzhydrol and 1.4 gr of t-BuOK were added to 25 ml benzene under a nitrogen atmosphere. The vessel was then immensed in liquid nitrogen and the entire system was degassed by several freeze-pump-thaw cycles. The solution was warmed-up at room temperature and dry $^{18}O_2$ (95.2% purity, the Heavy Oxygen Separation Plant, The Weizmann Institute of Science) was transferred from a gas buret equipped with greaseless stopcorks which was driven by dry benzene. The reaction was allowed to proceed at room temperature for 1 hr (260 ml O_2 absorbed). The yellow precipitate was filtered over glass filter plate under a dry nitrogen atmosphere and washed thoroughly several times with dry benzene. After drying under vacuum resulted ca. 800 mg KO_2. The isotopic assay was acomplished by hydrolizing KO_2 with H_2O followed by mass-spectral analysis of the released gas. A content of 91.5% ^{18}O was obtained, which reflected the minimum enrichment of KO_2 in ^{18}O. The KO_2 content in the product obtained is 90 ± 2% as determined by measurement of the O_2 evolution (on samples identically prepared with isotopically normal oxygen).

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