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Karl Christe (ERC), et al., "Improved Synthesis of CsN_3"

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Improved Synthesis of CsN_3

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Dedicated to Professor Joachim Straehle on the occasion of his 65th birthday

Abstract. Cesium azide can conveniently be prepared from anhydrous CsF and $(CH_3)_3SiN_3$ in SO_2 solvent in high purity and yield. In this reaction, the initially generated SO_2F^- anion is converted in SO_2 solvent to solvated azide, $(SO_2)_nN_3^-$, which is labile and releases SO_2 under dynamic vacuum yielding pure CsN_3.

Keywords: Cesium azide; Fluorosulfite; Azidosulfite

Verbesserte Synthese von CsN_3

Inhaltsübersicht. Cäsiumazid kann bequem durch die Reaktion of wasserfreiem CsF und $(CH_3)_3SiN_3$ in SO_2 Lösung in hoher Reinheit und Außbeute dargestellt werden. In dieser Reaktion wird das zuerste bebildete SO_2F^- Anion in SO_2 Lösung zu dem solvatisierten Azid, $(SO_2)_nN_3^-$, konvertiert, welches im dynamischen Vakuum labil ist und unter SO_2 Verlust reines CsN_3 liefert.

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Introduction

Sodium azide is a widely used reagent and is technically prepared form $NaNH_2$ and N_2O [1]. The heavier alkali metal azides are generally prepared starting from NaN_3. Two general methodologies for the preparation of heavier alkali metal azides such as CsN_3 have been employed. The most common preparative route utilizes an aqueous solution of HN_3 which is neutralized by the corresponding alkali metal hydroxide or carbonate [2-4]. Aqueous HN_3 is generally prepared from NaN_3 and H_2SO_4 [2]. In the second approach, cesium and rubidium azide have been prepared via ion exchange chromatography starting from aqueous NaN_3 [5]. Since the handling of HN_3 is potentially hazardous, a facile synthetic route to CsN_3 without the use of HN_3 is highly desirable. Circumventing the use of HN_3 and laborious chromatographic techniques, $[N(CH_3)_4][N_3]$ has been prepared from $[N(CH_3)_4][F]$ and $(CH_3)_3SiN_3$ in CH_3CN solvent [6]. In the present note, we present a new facile laboratory preparation of CsN_3 starting from $(CH_3)_3SiN_3$ and CsF in SO_2 solvent.

Results and Discussion

In analogy to the synthesis of $[N(CH_3)_4][N_3]$, the preparation of CsN_3 was attempted from anhydrous CsF and excess $(CH_3)_3SiN_3$ in refluxing CH_3CN solvent. The reaction in CH_3CN solvent was found to be slow and did not yield pure CsN_3 even after five days. The reaction of CsF with neat $(CH_3)_3SiN_3$ was also found to be slow; even after three days at temperatures close to the boiling point of $(CH_3)_3SiN_3$ (93 °C) significant amounts of CsF were still present. The sluggishness of these reactions is presumably a consequence of the insufficient solubility of CsF in CH_3CN and $(CH_3)_3SiN_3$. The removal of $(CH_3)_3SiF$ and addition of fresh $(CH_3)_3SiN_3$ did not result in a significantly faster conversion, indicating either the absence of an equilibrium reaction or a coating of the starting material by the product.

Anhydrous CsF reacts with SO_2 solvent to the fluorosulfite anion, SO_2F^- (eq. (2)) [7]. The reaction of $[Cs][SO_2F]$ suspended in SO_2 with excess $(CH_3)_3SiN_3$ results in complete azide-fluoride exchange within less than one hour yielding a clear, yellow solution of $[Cs][(SO_2)_nN_3]$ according to eq. (2).

$$CsF + SO_2 \longrightarrow [Cs][SO_2F] \qquad (1)$$

$$[Cs][SO_2F] + (CH_3)_3SiN_3 + nSO_2 \xrightarrow{SO_2} [Cs][(SO_2)_{n+1}N_3] + (CH_3)_3SiF \quad (2)$$

Removal of the volatiles (SO_2 and $(CH_3)_3SiF$) at ambient temperature results in precipitaiton of yellow $[Cs][(SO_2)_2N_3]$ which is converted to $[Cs][SO_2N_3]$ and $[Cs][N_3]$ upon prolonged pumping [8]. Pure $[Cs][N_3]$ is obtained after SO_2 removal under dynamic vacuum at 55 °C yielding a white solid. Since $[Cs][SO_2F]$ does not lose SO_2 at 55 °C, the complete conversion of SO_2F^- to N_3^- can be verified by the absence of signals associated with the SO_2F^- anion in the Raman spectrum.

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Experimental

Materials and Apparatus. All volatile materials were handled in a Pyrex vacuum line equipped with Kontes Teflon valves. Nonvolatile materials were handled in the dry argon atmosphere of a dry box.

The solvents, CH_3CN (Baker) and SO_2 (Aldrich, >99.9%) were dried over P_4O_{10} and CaH_2 and were freshly distilled prior to use. The CsF (KBI) was fused in a platinum crucible, transferred while hot to the dry box, and finely powdered. Trimethylsilyl azide

(Aldrich, 95%) was purified by fractional condensation through cold traps held at -35 and -196 °C and using the -196 °C fraction.

Preparation of CsN_3. In a typical reaction, anhydrous CsF (2.952 g, 0.0194 mol) was suspended in 8.861 g SO_2 at room temperature inside a glass vessel equipped with a Kontes valve. Excess trimethylsilyl azide (2.754 g, 0.0239 mol) was condensed onto the frozen reaction mixture at -196 °C. Upon warming to room temperature, the solid phase turned yellow and dissolved in the liquid SO_2 within 40 min, yielding a two-phase system consisting of a lower yellow and an upper colorless layer. Volatiles were removed under dynamic vacuum at ambient temperatures for approximately 30 min. yielding a yellow solid. Further pumping at 50 to 55 °C for ca. 2 hours yielded pure, colorless $[Cs][N_3]$ (3.400 g; 0.0194 mol).

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