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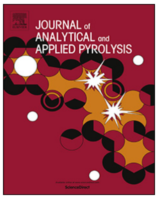

Flash vacuum pyrolysis of sulfamoyl azides and chlorides: Facile gas-phase generation of transient *N*-sulfonylamines

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ABSTRACT

Two sulfamoyl azides, $H_2NS(O)_2N_3$ and $MeN(H)S(O)_2N_3$, have been isolated as neat substances and characterized. The solid-state structure of the parent molecule $H_2NS(O)_2N_3$ has been established with X-ray crystallography. The thermal decomposition of both azides has been studied by combining flash vacuum pyrolysis (FVP, 400 °C) and matrix-isolation IR spectroscopy. In addition to the complete dissociation fragments for $H_2NS(O)_2N_3$ (SO_2, N_2, and H_2) and $MeN(H)S(O)_2N_3$ (SO_2, N_2, and CH_2NH), the retro-ene decomposition products HN_3 and *N*-sulfonylamines $HNSO_2$ and $MeNSO_2$ form, respectively. Alternatively, quantitative yield of both *N*-sulfonylamines in the gas phase occurs when sulfamoyl chlorides $H_2NS(O)_2Cl$ and $MeN(H)S(O)_2Cl$ are used as the FVP precursors (400 °C). Consistent with these experimental observations, computational studies on the potential energy profiles for the decomposition of the two azides at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(3df,3pd) level conclusively suggest that the N_2-elimination is energetically more favorable than the HN_3-elimination through either retro-ene reaction or 1,2-elimination. In contrast, the facile HCl-elimination from sulfamoyl chlorides provides a general method for the gas-phase generation of *N*-sulfonylamines, which were known as transient reactive intermediates in synthetic chemistry.

1. Introduction

Sulfonyl azides, $RS(O)_2N_3$, are versatile reagents in organic synthesis, such as the copper(I)-catalyzed azide–alkyne cycloadditions (CuAAC) for the synthesis of *N*-sulfonyl-1,2,3-triazoles [1], the transition metal catalyzed C–H amidations and enantioselective enzymatic C–H aminations for synthesis of biologically relevant sulfonamides [2], and the colbalt(II)-catalyzed intramolecular C–H amination and aziridination for the synthesis of diamines [3–5]. Similar to carbonyl azides ($RC(O)N_3$) [6–8], phosphoryl azides ($R_2P(O)N_3$) [9–11], and sulfinyl azides ($RS(O)N_3$) [12,13], most sulfonyl azides are energetic and may decompose explosively through molecular nitrogen extrusion upon either pyroysis or photolysis. Hence, sulfonyl azides are usually used as in situ reagents, and only very few sulfonyl azides such as $FS(O)_2N_3$ [14], $MeS(O)_2N_3$ [15], and $O_2S(N_3)_2$ [16] have been isolated as neat substances and structurally characterized.

As one of the most fundamental reactions of all covalent azides, the decomposition of various alkyl- and aryl-substituted sulfonyl azides in cryogenic matrices, gas phase, and solution has been intensively explored by using matrix-isolation, time-resolved spectroscopy, chemical trapping, and quantum chemical calculations in the recent few years [17–19]. The combined experimental and computational results demonstrate that the decomposition depends strongly on the substituent. For instances, thermolysis of gaseous $FS(O)_2N_3$ mainly yields N_2 and the thermally robust sulfonyl nitrene $FS(O)_2N$ [20], whereas, the thermal decomposition of $CF_3S(O)_2N_3$ furnishes complete fragments N_2, $\cdot CF_3$, and $\cdot NSO_2$ [21]. The flash vacuum pyrolysis (FVP) [22,23] of $PhS(O)_2N_3$ provides an alternative method for the generation of the fundamentally important phenylnitrene PhN [24,25] with concomitant N_2 and SO_2 elimination [26]. And, the FVP of $MeOS(O)_2N_3$ yields the simplest *N*-sulfonylamine $HNSO_2$ via the concerted fragmentation of the sulfonyl nitrene intermediate $MeOS(O)_2N$ ($\rightarrow HNSO_2 + H_2CO$) [27]. Nevertheless, the decomposition of all these azides $RS(O)_2N_3$ invariably involves the initial formation of the sulfonyl nitrenes $RS(O)_2N$ by N_2-elimination, as followed by diverse secondary reactions of the nitrenes such as dimerization, pseudo-curtius-rearrangement to *N*-sulfonylamine $RNSO_2$, or direct dissociation to radicals $R\cdot$ and $\cdot NSO_2$.

In contrast, the decomposition of sulfamoyl azides $R_2NS(O)_2N_3$ is rather limited, which is consistent with the recent description given by Culhane and Fokin that sulfamoyl azides make only fleeting appearance in organic synthesis [28]. More recently, sulfamoyl azides, readily generated from either sulfamoyl chlorides with sodium azide [29] or

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secondary amines with imidazolium triflate [28], have found increasingly broad applications as in situ reagents for the synthesis of 1-sulfamoyl-1,2,3-triazoles [30], 1,3-diamines [31], α-amino acid derivatives [32,33]. As the parent molecule, $H_2NS(O)_2N_3$ was first synthesized by Shozda and Vernon in 1967 and incompletely characterized by IR, NMR, and mass spectroscopy, and it has mechanical shock sensitivity comparable with that of nitroglycerin [34]. Very recently, the thermal decomposition of a number of sulfamoyl azides bearing at least one benzyl-substituent on the nitrogen atom was studied in solution [35]. It was found that the azides $R^1R^2NS(O)_2N_3$ decompose to form C—C bond by breaking two C—N bonds with simultaneous production of SO_2 and N_2. The mechanistic study indicates that the decomposition goes through a Curtius-type rearrangement of the sulfamoylnitrene $R^1R^2NS(O)_2N$ to the unstable *N*-sulfonylamine $R^1R^2NNSO_2$, which dissociates immediately and forms C—C bond through the dissociation of the putative 1,1-diazene R^1R^2NN. More recently, the photolytic decomposition of sulfamoyl azides in cryogenic matrices (< 10 K) was studied, the key dissociation intermediate sulfamoyl nitrenes were directly observed with IR and EPR spectroscopy [29]. Whereas, the thermal decomposition of sulfamoyl azides in the gas phase remains hitherto unexplored.

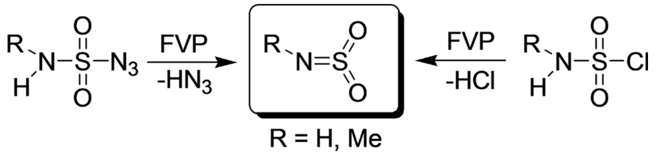
Continuing our interest in the structure and reactivity of simple covalent azides (e.g., $CF_3S(O)N_3$ [12], $NH_2C(O)N_3$ [36,37], and $CF_3C(O)N_3$ [38]), herein, we report a first-time full spectroscopic and structural characterization of the simplest sulfamoyl azide $H_2NS(O)_2N_3$ and its *N*-methyl derivative $MeN(H)S(O)_2N_3$. Moreover, the thermal decomposition of both sulfamoyl azides and the closely reacted chlorides in the gas phase has been studied by combining FVP and matrix-isolation IR spectroscopy, and the underlying mechanism has been also uncovered by quantum chemical calculations. And, a new and safe method for the gas-phase generation of transient *N*-sulfonylamines $RNSO_2$ (R = H and Me) by using sulfamoyl chlorides rather than explosive azides has been disclosed (Scheme 1). It should be noted that the elimination of HCl from sulfamoyl chlorides $EtN(H)S(O)_2Cl$ with triethylamine in solution was known to occur even at −78 °C [39], the transient intermediate *N*-sulfonylamines were in situ trapped by nucleophile as Burgess reagents that found broad applications in the synthetic organic chemistry [40–42].

2. Experimental section

Caution! Covalent azides are potentially hazardous explosive. Although we have not experienced any incident during this work, safety precautions (face shields, leather gloves, and protective leather clothing) are recommended for handling the azides.

2.1. Sample preparation

Sulfamoyl azides ($H_2NS(O)_2N_3$) was prepared according to the reference with modifications [34]. Briefly, a solution of 12 mmol freshly purified sulfamoyl chloride ($H_2NS(O)_2Cl$) in 4 ml of acetonitrile (CH_3CN) was added to a stirred mixture of 18 mmol sodium azide (NaN_3) in 4 ml of CH_3CN. The reaction was completed after 48 h at 45 °C. After filtration, the solvent was evaporated in vacuum. Then the residue was purified by trap-to-trap condensation (0, −95, and −196 °C) in dynamic vacuum (10 Pa). The product $H_2NS(O)_2N_3$ was collected in the 0 °C trap as white solid. Its purity was checked by ^1H (δ = 5.43 (s, 2H, NH_2) ppm) NMR spectroscopy. 1-^{15}N sodium azide (98 atom % ^{15}N, EURISO-TOP GmbH) was used for the preparation of ^{15}N labeled sample.



Scheme 1. Flash Vacuum Pyrolysis of $RN(H)S(O)_2N_3$ and $RN(H)S(O)_2Cl$ (R = H, Me).

N-methylsulfamoyl azide ($MeN(H)S(O)_2N_3$) was prepared according to published protocols with modifications. Which is in the similar manner to that of $H_2NS(O)_2N_3$. Briefly, a solution of 14 mmol freshly purified *N*-methylsulfamoyl chloride ($MeN(H)S(O)_2Cl$) in 4 ml of CH_3CN was added to a stirred mixture of 20 mmol NaN_3 in 4 ml of CH_3CN. The reaction was completed after 48 h at 50 °C. After filtration, the solvent was evaporated in vacuum. Then the residue was purified by repeated trap-to-trap condensation (−40, −95, and −196 °C) in dynamic vacuum (10 Pa). The product $MeN(H)S(O)_2N_3$ was collected in the −40 °C trap as colorless liquid. Its purity was checked by ^1H NMR (400 MHz, $CDCl_3$, δ = 5.20 (s, 1H, NH), 2.92 (d, J = 5.2 Hz, 3H, CH_3) ppm) and ^{13}C NMR spectroscopy (400 MHz, $CDCl_3$, δ = 30.29 (s, CH_3) ppm).

2.2. Matrix IR spectroscopy

The gaseous sample was mixed by passing a flow of Ne gas through a U-trap containing ca. 30 mg of the azide or chloride. Then the mixture (sample/Ne ≈ 1:1000 estimated) was passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), which can be heated over a length of ca. 25 mm by a tantalum wire (o.d. 0.4 mm, resistance 0.4 T) and immediately deposited (2 mmol/h) at a high vacuum onto the Rh-plated copper block matrix support (2.8 K) in a high vacuum (~10^{-6} Pa). While not directly measured, the expected residence time of the mixture in the pyrolysis tube is about a few milliseconds, and the pressure inside the pyrolysis tube is about 10 mbar. The electric power (voltage/current) used in the pyrolysis experiments was 3.5 V/3.03 A. Photolysis experiments were performed using an ArF excimer laser (Gamlaser EX5/250, 3 Hz).

2.3. X-ray crystallography

Crystals of $H_2NS(O)_2N_3$ were grown in a U type glass tube (o.d. 0.8 cm, length 15 cm, width 3 cm). Briefly, a small amount of the freshly purified sample (ca. 10 mg) was condensed into the upper part of one side of the glass tube at the ice-water. As the lower melting point (29 °C) of the azide, a suitable crystal of $H_2NS(O)_2N_3$ was quickly selected at ca. 3 °C under the microscope, followed by a quick transfer of the crystals onto the X-ray instrument. Crystals were mounted on Cryoloops with Paratone and optically aligned on a Bruker D8-Venture single-crystal X-ray diffractometer equipped with a digital camera. For the data collection, the Turbo X-ray Source (Mo Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector under 273(2) K were used. The structure was solved by direct methods and refined on F^2 by full-matrix least squares methods using SHELXL [43]. All of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were put in calculated positions. The graphics were drawn by using the Diamond software package [44]. CCDC 1849506 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

2.4. Computational details

Structures and IR frequencies of stationary points and transient states were calculated using the DFT methods (B3LYP [45–47] and M06-2X [48]) with the 6-311 + +G(3df,3pd) basis set [49–51]. Accurate energies calculation were performed using ab initio CCSD(T) methods [52,53] with the aug-cc-pVTZ basis set [54,55] and CBS-QB3 [56], respectively. Transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations [57]. All reaction energies calculated at the CCSD(T)/aug-cc-pVTZ level are corrected with zero-point energy (ZPE) at the B3LYP/6-311 + +G(3df,3pd) level. All the