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# An *ab initio* CBS-QB3 quantum chemical study of singlet and triplet sulfonylnitrenes insertion into acetylenes and nitriles

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## ABSTRACT

The reactions of methylsulfonylnitrene **1a** and trifluoromethylsulfonylnitrene **1b** with acetylene **2**, dimethylacetylene **3**, acetylenedicarboxylic acid **4**, hydrogen cyanide **5**, acetonitrile **6**, cyanoformic acid **7** were studied theoretically at the CBS-QB3 level of theory. The main products of the reaction of triplet sulfonylnitrenes **3** with alkynes **2–4** are 1,2,3-oxathiazole 2-oxides **10** formed from triplet diradical adducts after intersystem crossing (ISC) to their singlet spin-isomers. Products **10** are also formed from singlet nitrenes **1** along with *N*-vinylidenesulfonamides **9** and 1-(alkylsulfonyl)-1*H*-azirines **11**. The latter, being antiaromatic, isomerize exothermically to 2-(alkylsulfonyl)-2*H*-azirines **12**. In a similar way, both singlet and triplet sulfonylnitrenes **1** react with nitriles **5–7** to give 1-(alkylsulfonyl)-1*H*-diazirines **16**. With singlet nitrenes, nitriles **5–7** can also react with the formation of 2-(methylidyne)-1-(alkylsulfonyl)diazan-2-ium-1-ides **14**, which undergo either intramolecular 1,3-cyclization to 3-(alkylsulfonyl)-3*H*-diazirines **17** or intramolecular 1,5-cyclization to 1,2,3,4-oxathiadiazole 2-oxides **15**. Relative stability of the key products and activation barriers of their interconversion are discussed.

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## 1. Introduction

Recently, there has been a growing interest to investigation of chemical transformations of highly reactive short-living intermediates, based on such powerful tools in the hands of organic chemists as laser flash photolysis and pico- and femto-second time-resolved UV–Vis–IR-spectroscopy [1–3]. The objects of the present study – sulfonyl nitrenes – belong to this very category of fleeting species existing on the timescale of pico- to microseconds. In sulfonylnitrenes the sextet nitrogen atom is covalently bound to the sulfonyl group; the ground state is triplet, whose lifetime is measured by microseconds [3–5], while its singlet spin counterpart with the lifetime of hundreds of picoseconds [6–8] is more reactive [3].

The formation, spectroscopic characterization and transformations of sulfonyl nitrenes were recently studied for CH<sub>3</sub>SO<sub>2</sub>N,

its fluorinated analogue CF<sub>3</sub>SO<sub>2</sub>N and arylsulfonylnitrenes (2-naphthyl-, *p*-tolyl- and 4-bromobenzenesulfonylnitrenes) by femtosecond time-resolved IR spectroscopy [6,7], and matrix isolation [9–11].

For both nitrenes CH<sub>3</sub>SO<sub>2</sub>N and CF<sub>3</sub>SO<sub>2</sub>N only triplet ground state was experimentally observed. It has been shown that triplet CH<sub>3</sub>SO<sub>2</sub>N has the formation time constant of 34 ± 3 ps in dichloromethane [7]. When isolated in solid Ne-matrix, triplet CH<sub>3</sub>SO<sub>2</sub>N demonstrates the two strongest IR bands at 1349.8 and 1156.6 cm<sup>-1</sup> belonging to ν<sup>as</sup>(SO<sub>2</sub>) and ν<sup>s</sup>(SO<sub>2</sub>) [10]. In case of the similarly isolated triplet nitrene CF<sub>3</sub>SO<sub>2</sub>N, two band at 1389.8 and 1179.8 cm<sup>-1</sup> appear in the IR spectrum, along with the bands of the Curtius-like photoproducts CF<sub>3</sub>NSO<sub>2</sub>, CF<sub>3</sub>S(O)NO, CF<sub>2</sub>NSO<sub>2</sub>F and SO<sub>2</sub>. The first Curtius-like photoproduct was also observed after subsequent UV irradiation of the matrix-isolated triplet CH<sub>3</sub>SO<sub>2</sub>N [10]. Moreover, both triplet nitrenes CH<sub>3</sub>SO<sub>2</sub>N and CF<sub>3</sub>SO<sub>2</sub>N were directly detected by the ESR spectroscopy at low temperatures [9,12]. Being stable in triplet ground state, sulfonyl nitrenes are characterized by medium singlet-triplet energy gap ΔE<sub>ST</sub> of 14–18 kcal/mol at the DFT and CCSD(T) level of theory with

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different basis sets [6,10,13], significant expansion of basis set (MP2/aug-cc-pVTZ, CBS-QB3) resulting in a decrease of  $\Delta E_{ST}$  to 5–8 kcal/mol [13–15].

It is worth mentioning, that sulfonyl nitrenes, as well as carbonyl-, phosphinyl- and phosphoryl nitrenes, have low-lying closed-shell singlet state [3]. Stabilization of such electronic configuration is associated with intramolecular bonding interaction between O and N atoms. Only in the case of acylnitrenes such interaction results in lowering the singlet state which become the ground state [8].

Thus, sulfonyl nitrenes in the singlet state display strong electrophilic properties and can insert into H–X bonds, where X=C, N, O, etc. [16,17], or synchronously add to C=C double bonds affording aziridines [17–20]. In contrast, in the triplet state, sulfonylnitrenes act as diradicals [16] and are capable of H-abstraction [3].

The formation of aziridines by the addition of nitrenes to alkenes is well studied and is used in laboratory practice as a preparative method for their synthesis [20]. The addition of nitrenes, as electrophilic species, to one of the  $\pi_{C=C}$  bonds of alkynes or of the  $\pi_{C=N}$  bonds of nitriles is much less studied, although very interesting from a mechanistic point of view. In the literature, we have found only two examples of addition of nitrenes to acetylenes [21,22]. The first was the addition of phthalimidonitrene to acetylenes to give 1*H*-azirines and spontaneous rearrangement of the latter to the 2*H*-isomers (5–15% yield) reported as early as in 1969 [21]. The formation of oxazoles by 1,3-dipolar cycloaddition of acylnitrenes to acetylenes or via transient 1*H*-azirines was also reported [22,23]. In both cases, the singlet nitrenes were the active species, suggesting the possible concerted nitrene insertion into the triple bonds of alkynes and initial 1*H*-azirines formation. Noteworthy, the addition of phthalimidonitrene to phenylbutenyne containing both double and triple bonds proceeds exclusively at the double bond, which was attributed to the antiaromatic transition state for the addition to the triple bond [24].

The photolysis of *p*-trimethylsilylbenzoyl azide in acetonitrile in the presence of diphenylanthracene affords isocyanate and 3,4-oxadiazole, the product of reaction of the singlet aroyl nitrene with the solvent [3,25,26]. More careful investigation using time-resolved IR spectroscopy showed the formation of ylide PhC(O)N–N≡CD<sub>3</sub> during the photolysis of benzoyl azide in argon-saturated acetonitrile-*d*<sub>3</sub> with the rate constant  $3.2 \times 10^6 \text{ s}^{-1}$ . The ylide then suffers intramolecular cyclization to give 3,4-oxadiazole with the rate constant  $4.3 \times 10^4 \text{ s}^{-1}$  [3,27]. The formation of ylides was also found in the photolysis of *N*-acetyldibenzothiophene sulfilimine in acetonitrile-*d*<sub>3</sub> [3,28]. We failed to find any data in the literature on the reactions of sulfonylnitrenes with acetylenes or nitriles.

In continuation of our computational and experimental studies of sulfonylnitrenes [7,14,15,28,29] we report here the results of theoretical calculations of the reaction of methylsulfonylnitrene (**1a**) and trifluoromethylsulfonylnitrene (**1b**) with acetylene (**2**), dimethylacetylene (but-2-yne) (**3**), acylenedicarboxylic (but-2-ynedioic) acid (**4**), hydrogen cyanide (formonitrile) (**5**), acetonitrile (**6**), cyanofornic acid (**7**) using the CBS-QB3 composite method in order to throw light on the mechanism and thermodynamics of the reactions as well as to assess the effect of the substituents in the reagents. For simplicity, the reactions which do not include the triple bond, such as H-abstraction or X–H insertion, are omitted from consideration.

## 2. Experimental section

All calculations were performed using the high-level composite CBS-QB3 method of Petersson et al. [30,31] (if not otherwise stated)

using the Gaussian 09 suite of programs [32]. For each stationary point, the second derivatives of the energy with respect to the Cartesian nuclear coordinates were calculated to confirm whether these structures were local minima or transition states (included by default into CBS-QB3 methodology in Gaussian 09). Geometry optimization for transition states was first performed with the Becke's three-parameter exchange functional in combination with the Lee-Yang-Parr correlation functional, B3LYP, employing 6-311G (2d,d,p) (CBSB7) basis set (as the first step of CBS-QB3 method) followed by "normal" CBS-QB3 calculation. All transition state calculations were accompanied by intrinsic reaction coordinate (IRC) calculations [33] to verify that each transition state connected the corresponding reactants and products.

A search for singlet diradical intermediates from the triplet sulfonylnitrenes and acetylenes or nitriles was implemented as described previously [15,28]. Briefly, the triplet diradical structure optimized at the UB3LYP/CBSB7 level of theory was taken for single point energy unrestricted wave function calculations utilizing singlet multiplicity at (i) UB3LYP/CBSB7 including the second derivatives of the energy computation, (ii) UCCSD(T)/6-31 + G (d'), (iii) UMP4SDQ/CBSB4 and (iv) UMP2/CBSB3 with the minimum number of pair natural orbitals equal to ten and localization based on populations in minimal basis (by default). Then, the obtained energies were treated as described in Ref. [30] to obtain final CBS-QB3 energies. All energy parameters discussed throughout the discussion section refer to ZPE corrected total CBS-QB3 energies ( $\Delta E$ ) if not stated otherwise.

The comparative analysis of total energies of all intermediates involved in the mechanism of acetylene and formonitrile attack by methylsulfonyl nitrene obtained at CBS-QB3 level of theory and some other methods (B3LYP/CBSB7, PBE1PBE/6-311++G\*\*, wB97XD/6-311++G\*\*, CCSD(T)/6-31 + G (d')/B3LYP/CBSB7, MP4SDQ/CBSB4//B3LYP/CBSB7, MP2/CBSB3//B3LYP/CBSB7) is described in Appendix A. Supplementary data. All the optimized geometries are also available in there.

## 3. Results and discussion

### 3.1. Addition of sulfonylnitrenes to acetylene

To simulate the addition of singlet sulfonylnitrenes CH<sub>3</sub>SO<sub>2</sub>N (**1a**) and CF<sub>3</sub>SO<sub>2</sub>N (**1b**) to one of the  $\pi_{C=C}$  of acetylene (**2**), the ghost atom (Bq) was added and both Bq···C distances were fixed to 1.400 Å; then the Bq···N distance was decreased stepwise, other geometrical parameters being optimized. The result of the scanning was the formation of 1-(methylsulfonyl)-1*H*-azirine (**11a**) or 1-(trifluoromethylsulfonyl)-1*H*-azirine (**11b**) (Scheme 1). The formation of products **11** is barrierless with the energy of the system ( $\Delta E$ ) decreased by –62.5 (**11a**) or –65.7 kcal/mol (**11b**), respectively (Table 1). 1*H*-Azirines **11** are rather unstable due to antiaromatic character of the cyclic fragment of the molecule with four  $\pi$ -electrons [21,34,35].

Another issue of stability of 1*H*-azirines is their quite tight structure in comparison with the corresponding aziridines [36]. Indeed, the formation of aziridines from nitrenes **1a** or **1b** and ethylene is by 20–25 kcal/mol more endothermic than the formation of 1*H*-azirines **11** from the same nitrenes and acetylene [15]. The latter are more reactive species capable of transformation to 2*H*-azirines **12**; that is why 2*H*-azirines are usually registered as the products of the reaction of nitrenes with acetylenes, while 1*H*-azirines **11** are considered as unstable intermediates [21]. The molecules of 2*H*-azirines **12** are neither aromatic nor antiaromatic because of the presence of *sp*<sup>3</sup>-hybridized carbon atom in the ring. This results in a decrease of their relative energy by ~27 kcal/mol with respect to the corresponding antiaromatic 1*H*-azirines **11**, in

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