



Account/Revue

Disulfonyl carbon acids – synthesis, spectroscopic and structural studies – a review

Iwona Binkowska

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89 b, 61-614 Poznań, Poland

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ABSTRACT

The subject of carbon acids activated by two sulfonyl groups is reviewed. It will be shown that the studied compounds are relatively strong acids that have their importance in organic chemistry. The structure and reactivity of the products of the deprotonation reaction are also described. Structural studies using X-ray and spectroscopic methods such as IR, NMR or MS give more information about their proton donor properties. They are supplemented by charge distribution research in these carbanions using empirical evaluation and electron density *ab initio* calculation. A comparison of the results obtained for the title compounds with data obtained for other carbon acids activated by nitro or cyano groups is presented.

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1. Introduction

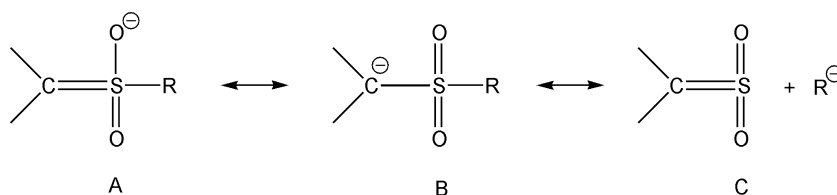
Sulfones represent an important class of organic compounds with pharmacological activity and technological applications. This functional group has been studied as a synthetic intermediate in organic synthesis since it can be readily removed from the substrate [1–3]. As can be seen in the literature, sulfonyl carbanions can be alkylated or acylated, and hence are a relevant reagent for C–C bond formation [4–6]. Carbanions that are stabilized by carbonyl, cyano, nitro, and sulfonyl groups have a wide range of uses. Generally, carbanions with localized charge should be tetrahedral, and carbanions whose charge is delocalized should be planar. Elements such as sulfur, phosphorus, and halogens (except fluorine) contain d orbitals, and then are capable of delocalizing and stabilizing the negative charge. It is believed that carbanions containing cyano or sulfonyl groups are closer to “true carbanions” in comparison with carbanions activated by the nitro group, where the negative charge is delocalized on the oxygen atoms of the nitro group.

Thus, the anion formed after the deprotonation of nitroalkane is stabilized by the electronic shift from the carbon atom to the nitro group. It is well known as nitroalkane anomaly [7–11]. Nitroalkanes show low intrinsic reactivity in protic solvent and normal or high in DMSO. On the other hand, in cyano carbanions the negative charge is localized on the acidic carbon acid [12]. It is known that the sulfonyl group is a strong electron-withdrawing group and then has the ability to stabilize the α -sulfonyl carbanion, but it is less clear how this stabilization takes place [13–15,7]. The delocalization of the negative charge away from carbon acid in an sp^2 hybridized carbanion with a $d_{\pi}-p_{\pi}$ bonding would involve a significant decrease in intrinsic rate constants compared with “normal acids”, i.e. a behavior typical of carbon acids activated by carbonyl or nitro groups. The role of the resonance effect due to a $d_{\pi}-p_{\pi}$ bonding between the carbanion lone pair and 3d orbital of sulfur (A) has been questioned by theoretical studies. The results of the computational study [16,17] suggested a rather simple charge polarization effect (B). Another factor influencing the stabilization of the negative charge is negative hyperconjugation (C). Resonance structures A, B and C of sulfonyl carbanion are shown in Scheme 1.

Email address: iwonalak@amu.edu.pl.

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Scheme 1. Resonance structures of sulfonyl carbanion.

The electron-withdrawing capability of the SO_2CF_3 group to stabilize the negative charge of the carbanion is the result of the polarizability effect. Goumont et al. [18] provided convincing experimental evidence of the unusually strong electron transmission ability of the highly acidifying SO_2CF_3 group, which was considered to be a consequence of its high polarizability. The SO_2CF_3 group seems to stabilize the excess negative charge via the polarizability effect while the resonance effect is very modest [18–20]. The sulfonyl group is more activating than the nitro one. The activation by the nitro group is favored in aqueous solution when solvation by hydrogen bonding stabilizes the nitronate anion. The situation is in contrast with the case of DMSO, when the stabilization of the polarizable negative charge occurs and favors the activation by a SO_2CF_3 group. This is consistent with totally different solvent dependences on the acidity of nitro and triflic carbon acids in H_2O –DMSO mixtures [13,19]. A support for these observations is the comparison of the Hammett substituent constants (σ) reported by Sheppard and Yagupolskii et al. [21] for the SO_2CF_3 and the nitro one. The σ parameter for the SO_2CF_3 group shows that it is the strong electron-withdrawing group. The σ values obtained from studies of the ionization of various acids, for instance benzoic acids or phenols, show that the SO_2CF_3 group is more activating than the nitro one. The σ_p values obtained for substituted benzoic acids are 0.96 and 0.81 for SO_2CF_3 and nitro groups, respectively [22]. The structural analogs of 2,4,6-tris (trifluoromethylsulfonyl) benzene derivatives have been studied, but it is worth mentioning that the electronic properties of the SO_2CF_3 group are similar to those of fluorosulfonyl, the SO_2F group, used in potentially biologically active sulfamides or netlike polymers [23]. The electron-withdrawing ability of the fluorosulfonyl group is nearly the same as that determined for the trifluoromethylsulfonyl one, but it is substantially higher than that of the nitro group, so aromatic sulfonyl fluorides can be involved in various processes of applied chemistry [24].

The investigations about the rates of deprotonation of disulfonyl carbon acids report that the rates of deprotonation of these species approach the rates of “normal” proton transfer from oxygen acids [25,26]. This observation is consistent with the negative charge in the carbanionic conjugate base being effectively localized upon carbon, with little resonance delocalization into sulfonyl groups. Aiken studied rate and equilibrium data for the deprotonation of a series of phenyl ring substituted phenyl[bis(ethylsulfonyl)]methanes in an aqueous solution. The kinetics show that the proton-transfer reaction indicates intrinsic rate constants that are three to four orders of

magnitude lower than for normal acids, suggesting a considerable degree of charge delocalization. The obtained results suggested that after the ionization of disulfonyl carbon acids, partial delocalization of the negative charge on the carbanion occurs. This effect is somewhat larger than for cyano carbon acids, but it is considerably smaller than for nitro or carbonyl carbon acids. The acidifying power of sulfonyl groups is attributable not simply to electrostatic stabilization, but partly also to a mesomeric effect. The degree of mesomerism is, however, uncertain, because part of the intrinsic barrier may derive from steric effects, as is also observed for bromination [26]. As regards the structures of carbanions activated by sulfonyl groups, only some of them have been described by NMR [13,18,19,27,28], IR [29–32], X-ray [33–40], computational [35–37,40–43], kinetic and thermodynamic [19,20,26,44–46] studies.

This paper aims at discussing the spectroscopic and structural approaches to the reactivity of carbon acids activated by two sulfonyl groups. This review is also an attempt to compile the literature on the subject of disulfonyl carbon acids and indicate the prospects for further research. The examples presented in this paper have shown that these carbon acids can be utilized in organic synthesis and are an important class of compounds. Despite the continuous interest in the problems of stabilization of carbanions and their applications in organic synthesis, there is a need for a review and summary of the achievements.

2. Synthesis of disulfonyl carbon acids

The synthesis of sulfones is of interest due to their valuable applications as intermediates during the preparation of various chemically and biologically important molecules [1]. Disulfonyl carbon acids can be prepared by several methods. The oxidation of sulfides is the most straightforward method for the synthesis of these compounds [1,47–50]. The synthesis of thioacetals using application Bunte salts (esters of sodium thiosulfuric acid) was first described by Wastlake and Dougherty [51]. In this process, sodium alkyl thiosulfates react with aldehydes in the presence of an acid to give thioacetals (Scheme 2). The obtained products can be oxidized resulting in the corresponding sulfone.

The oxidation of sulfides to sulfones was made using different oxidizing agents. Castro synthesized bis(methylsulfonyl)methane [6] using oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) as an oxidant under anhydrous conditions, described previously by Trost and Curran [52]. Aiken et al. [26] synthesized a series of bis(ethylsulfonyl)methanes

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