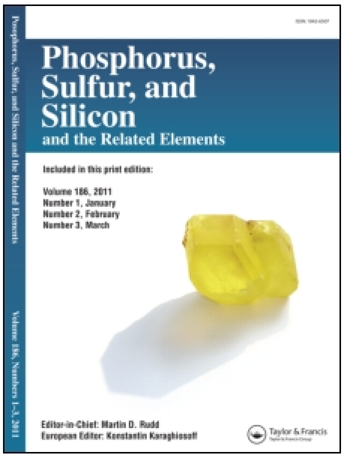

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THEORETICAL STUDY OF SULFINES AND SULFENES. SIMILARITIES AND DIFFERENCES IN STRUCTURE AND REACTIVITY. A NEW VIEW.

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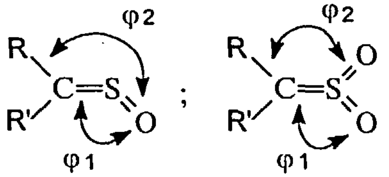
Abstract. Sulfenes and sulfines contrary to usual opinion can not be considered as structure-similar compounds.

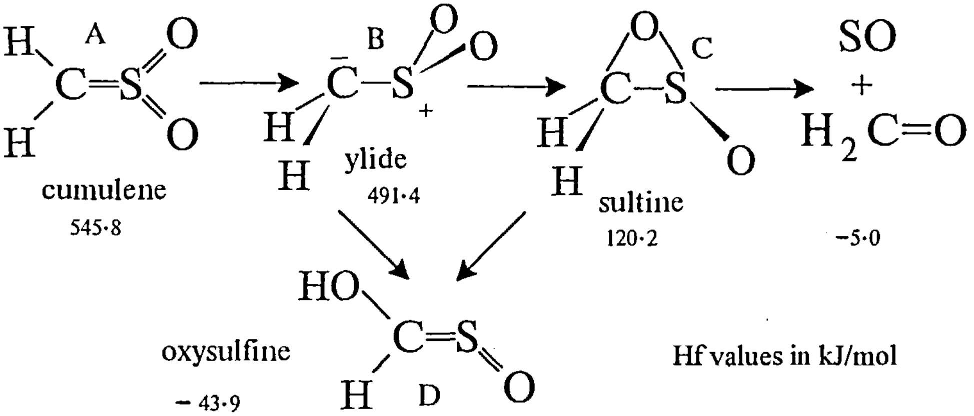
Heterocumulenes of sulfine (I) and sulfene (II) series (thioaldehyd S-oxides and S,S-dioxides) are very high reactive molecules acting as intermediates of acylation, electrophilic and nucleophilic addition, cycloaddition [1-4]. The overwhelming majority of works devoted to chemistry of these compounds are focused on methods of their preparation and directions of its synthetic use. At the same time, problems of comparative analysis of structures I and II, and also its reactivity have so far been given not enough attention. Sulfines and sulfenes were considered as structure-similar compounds.

A large number of compounds I [4] is known, whose stability at usual temperatures is sufficient for study of these molecules by physical and chemical methods. He- terocumulenes of sulfene serie are much less stable. The numerous attempts of their synthesis were a failure, therefore all knowledge about them were based only on indirect data (including sulfene trapping by amines in solution with zwitterion formation), as well as low-temperature IR-spectrum which has received by J.F.King [5]. Only recently we synthesised the first relatively stable sulfene [6] by using the stable Arduengo's carbene [7]. Unfortunately, the reasons for great difference in the stability of compounds I and II have so far remained incomprehensible. The aim of present work is the comparative quantum-chemical study of compounds I and II with R1,R2=H,F,Cl,Br,J (30 compounds). By the use of semi-empirical quantum chemical MNDO approximation the structure, MO, stability and isomerization routes of sulfines and sulfenes under a change of angles ∠CSO (φ_1) and ∠RCSO (φ_2) have been studied.



R, R' = H, F, Cl, Br, J

It was established that all the investigated sulfines have a planar structure with low energetic barriers of syn-anti isomerization (inversion mechanism, 15-30 kJ/mol). In the case of sulfenes the situation is much more complex: a) under $R_1=R_2=H$ the existence of "planar" sulfene is possible (Widberg's index of C-S bond is 1.45). But the change of φ_2 into 0.5 leads to isomerization of II into "ylide" sulfene. The potential energy surface of sulfene (under a change of angles φ_1 and φ_2) has a complex polyextremal character. It was found that process A⇒B⇒C has a very low barriers (<20kJ/mol) (Fig.1). The existence of isomers A, B and C was first postulated by Carlsen L. and J.P.Snyder [8] which however did not consider the routes of their isomerization.



Scheme 1.

b) under R_1=Hlg, R_2=H sulfenes have non-planar (i.e. ylide) structure (Widberg's index of C-S bond is 0.9, r(C-S)=1.8A); c) under R_1,R_2=Hlg only weak Van der Waals connection of $(Hlg)_2C$: and SO2 is observed (r(C-S)=3.5-4.5A). Only in case of joint steric and electronic stabilization the weak-stable sulfene may be synthesised [6] (r(C-S)=1.69A). Apparently, isomers A and B exist in equilibrium with a low inversion barrier. Structural dynamism of sulfene is a cause of it much higher reactivity in comparison with sulfine and compounds I and II can not be considered as structurally similar compounds. In our opinion, it would be more correct to consider sulfene as non-classic heterocumulenes. Being a binding link between heterocumulenes and ylides they can easily be "adapted" to specific situations arising as a result of chemical processes and lead to a wide range of existing reactions of these compounds.

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