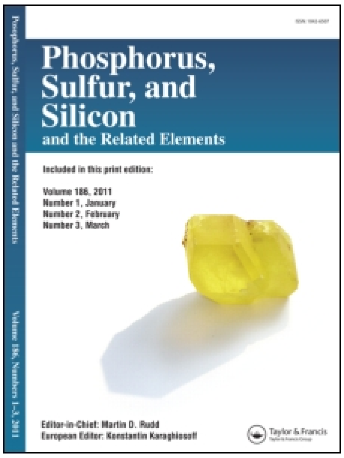

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A STANDARD DEFINITION OF THE TERM "THIIRANIUM ION"

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A STANDARD DEFINITION OF THE TERM "THIIRANIUM ION"

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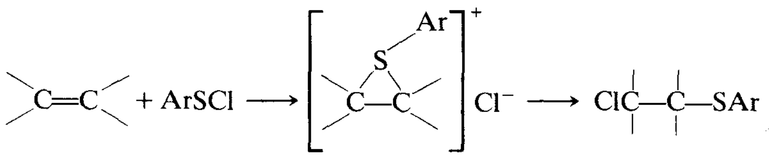
It is proposed that conventional nomenclature, based on that use for carbenium ions, be restored to the naming of thiiranium ions. Such a definition provides a general mechanistic classification for a large number of apparently diverse reactions while still allowing refinements to the mechanism in the form of thiiranium ion-pairs.

Key words: Thiiranium ions; definition; nomenclature.

There exists a difference of opinion in the chemical literature on the definition of a thiiranium ion. Originally, "Kharasch and Buess found that the additions (of arenesulfenyl chlorides [RSCl]) to various olefins are consistent with a mechanism involving the intermediate formation of an episulfonium ion intermediate"[1] (**1**, Equation 1). While Kharasch called this intermediate an episulfonium ion, the IUPAC name thiiranium ion is preferable today.



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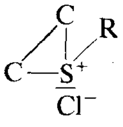
In 1979, Smit and co-workers[2] presented their view that "episulfonium ions are certainly not involved in the addition of RSCl to olefins under the usually accepted conditions". While accepting the formation of bridged intermediates such as **2** and **3** in the addition of arenesulfenyl chlorides to alkenes, Smit restricted the definition of a thiiranium ion to the species represented by **4**. Structure **4** corresponds to a bare or dissociated thiiranium ion in contrast to structure **1** proposed by Kharasch which specifically includes a chloride ion.



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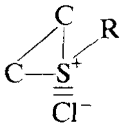

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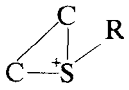

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The reasons cited by Smit for restricting the definition of a thiiranium ion to structure **4** are based on the reported differences in the products formed by thiiranium ions proposed as intermediates and those prepared as stable ions.

Thiiranium ions are proposed as intermediates in the (i) solvolysis of beta-chloroalkyl aryl sulfides, (ii) alkylation of thiiranes, and (iii) addition of alkane- and arenesulfenyl chlorides to alkenes.[3] Thiiranium ions can be prepared as stable ions by reactions that are variations of the reactions in which thiiranium ions are proposed as intermediates.[4] The difference is that to form a stable thiiranium ion, the counterion must be a very poor nucleophile to ensure that it will not react with the thiiranium ion.

The wide variety of reactions in which thiiranium ions are formed or proposed as intermediates raises the following question. Why should a stable thiiranium ion react in exactly the same way as a structurally identical thiiranium ion proposed as a reaction intermediate when the experimental conditions for the two reactions are so different? For example, the addition of arenesulfenyl chlorides to alkenes is usually carried out at room temperature in relatively nonnucleophilic and nonpolar solvents (acetic acid or chlorinated hydrocarbons). Stable thiiranium ions are usually prepared at low temperatures in more polar solvents (acetonitrile, nitromethane, and liquid sulfur dioxide). Thus it is not surprising that the products of the two reactions are different because the experimental conditions are not comparable. Therefore it is incorrect to use this difference to conclude that thiiranium ions are not involved in the mechanism of addition of arenesulfenyl chlorides to alkenes.

The fact that the reactions of a stable ion are not the same as those of the reactions of the structurally identical ion proposed as an intermediate is not unique to the chemistry of thiiranium ions. A similar situation exists in the chemistry of carbocations. For example, the reaction of 2-fluorobutane in SbF_5[5] or the reaction of 2-butanol in $HSO_3F—SbF_5—SO_2$ solution[6] forms the tert-butyl cation rather than the 2-butyl cation. The trifluoroacetolysis of optically active 2-butyl tosylate gives mainly optically inactive 2-butyl trifluoroacetate.[7] It would be wrong to conclude from these two reactions, carried out under very different experimental conditions, that a 2-butyl cation is not involved in the mechanism of the solvolysis because no tert-butyl trifluoroacetate is formed as product. The analogy with thiiranium ions is clear.

The original definition by Kharasch of a thiiranium ion and the more recent one by Smit can be reconciled by examining the work of Winstein on solvolysis reactions. Winstein developed a general solvolysis scheme involving a number of ion-pairs.[8] The carbocation portion of each of these ion-pairs was referred to by Winstein as varieties of carbonium ions.[9] It should be noted that the use of the word carbonium (or carbenium) ion in this context does not convey any information about the nature or location of the counterion. It simply tells us something about the structure of the cation involved.

In fact, chemists frequently write the structure of a carbenium ion in publications without even including the counterion as can be seen by a quick search of any chemical journal. But this does not mean that this structure represents a "free" or dissociated carbenium ion. Nor does it mean that the authors do not appreciate the importance of ion-pairs.

It seems logical that the current usage of the term carbenium ion should be extended to the term thiiranium ion. In this way, the term thiiranium ion would not convey any information about the counterion but it would tell us that the cationic portion of the intermediate or intermediates is a bridged species.

Using this definition and in keeping with Winstein's work, the cationic portions of the ion-pairs represented by structures **2**, and **3**, should all be called varieties of thiiranium ions. While there may be differences in the electronic structures of the cationic portion of **2** and **3**, they, as well as **1**, all conform to this definition of a thiiranium ion. The major difference between the thiiranium ions **2** and **3** is the location of their counter-ions. Thus structure **2** is a thiiranium contact ion pair while structure **3** is a thiiranium solvent separated ion-pair and **1** is a dissociated (or free) thiiranium ion.

It may seem like a very trivial matter whether the cationic portions of ion-pairs **2** and **3** are called thiiranium ions or not. But there are important reasons for attempting to standardize the use of the term thiiranium ion. Firstly this proposal is consistent with that used for carbocations. Secondly, it provides a general description of the structure of the cationic portion of the intermediate regardless of the nature and location of the counterion. This is important because usually it is not known if the cation exists as part of a contact ion-pair, solvent separated ion-pair or as a dissociated ion. Thus attention is focused on similarities of the mechanisms of a number of reactions. For example, any chemical reaction that involves species represented by structures **1–3** would be classified as one that reacts via a thiiranium ion mechanism. In contrast, using the narrower definition, only reactions involving ion **1** would be classified as those that react via a thiiranium ion mechanism.

Such a general and standardized definition of a thiiranium ion proposed here seems to be needed to avoid confusion in the literature. Two examples illustrate this point. Trost[10] has reported the functionalization of a double bond by the reaction of methylthio dimethyl sulfonium tetrafluoride with a number of alkenes followed by the reaction of the adducts with a variety of nucleophiles. Purrington[11] has reported the synthesis of beta fluoro thioethers by the reaction of alkenes with benzenesulfenyl chloride in the presence of silver fluoride. Both of these reactions introduce the groups RS and X (where X is fluorine or an oxygen or nitrogen containing group) across a double bond in an *anti*-stereospecific but nonregiospecific manner. We can say with some certainty that the mechanism of both of these reactions involve a thiiranium ion even though we have no information about the presence or absence of thiiranium ion-pairs. Yet the authors of these two papers were reluctant to come to this conclusion perhaps due to the confusion surrounding the use of the term thiiranium ion.

In conclusion, restoring the conventional definition of a thiiranium ion provides a general mechanistic classification. It recognizes similarities in the mechanism of a large number of apparently diverse reactions while still allowing refinements to the mechanism in the form of thiiranium ion-pairs.

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