A desulfonylation process as easy route for synthesis of 1,4-dinitro-1,3-dienes: Mechanistic study

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ABSTRACT

DFT calculations at different levels indicate a one-step nonpolar mechanism of the thermal decomposition of isomeric 2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxides. Formally, this process can be equivalent to retro [4+1]-cycloaddition reaction.

KEYWORDS

Desulfonylation; nitrodienes; mechanism; DFT calculations

GRAPHICAL ABSTRACT

Introduction

From a practical point of view, polynitro-1,3-dienes are important precursors in organic chemistry, so recently problems associated with their synthesis have strongly attracted the attention of organic chemists. It is known that elimination of small molecules is currently relatively the most universal method of the synthesis of unsaturated nitrocompounds. This process can be accomplished by different strategies. Some years ago, Berestovitskaya and coworkers showed that desulfonylation of 2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxide (1) gave via easy route (no catalyst used) corresponding 1,4-dinitro-1,3-diene (2):

It has to be noted that the molecular mechanism of these reactions has not been previously a subject of systematic studies. In the presented case, different theoretically possible mechanisms of conversion of reactants into products can be considered: (i) A single-step mechanism in which both S-C bonds are broken...
simultaneously, or alternatively; (ii) a single-step, but polar and asynchronous mechanism, wherein the S-C bonds break at different rates, and (iii) a zwitterionic mechanism, wherein in the first step only one C-S bond is broken – second bond break does not occur until the second reaction step:

Unfortunately, it cannot be a priori decided as to which of the above mechanisms will be realized in reality. However, it is known that a number of reactions, which until recently being considered pericyclic (single-stage), were proven later to be complex processes, often going through a step of ionic structures, either a ion-radical or a diradical. With this in mind, in the context of the present study were performed comprehensive quantum-chemical studies of a model reaction of decomposition of Z- (1a) and E-2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxides (1b). The studies were done for reactions in both gas phase and the simulated presence of dielectric media. This problem is very important from theoretical and practical points of view. In particular, in the case of one-step mechanism (i, ii), primary geometrical isomerism of substituents in 3 and 4 positions should be preserved. On the other hand, in the case of two-step reaction (iii) in post-reaction mixture isomeric dienes with different Z-E configuration may be obtained. In consequence, understanding the mechanism of the mentioned in the title reactions would allow to consciously plan synthesis of useful 1,4-dinitro-1,3-dienes in preparative organic chemistry.

Results and discussion

Energetical aspects

The analysis of energy parameters obtained by B3LYP/6-31G(d) calculations showed that decompositions of both Z- (1a) and E-2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxides (1b) are highly exothermic processes (Table 1). In case of desulfonylation, 1b changes in the free energy of the reaction, which is almost 22 kcal/mol, but in case of a corresponding reaction involving 1a, free energy change is more, being over 33 kcal/mol. Slightly more favorable thermodynamic conditions for the decomposition process of 1a (as compared with 1b) are evidently linked to a relatively lower thermodynamic stability of a more crowded heterocyclic 1a. It should be noted at this point that similar conclusions lead the calculations done with more advanced basis sets 6-31G(d,p), 6-31+G(d), and 6-311G(d).

Next, we analyzed the effect of environment polarity on the position of thermodynamic equilibrium within the reaction system. It turned out that in the presence of a weakly polar medium (toluene, ε = 2.374) and in a highly polar medium (nitromethane, ε = 36.562), the equilibrium of the process is shifted toward products’ side as much as it was in the case of gas phase reaction.

Detailed analysis of the reaction energy profiles has shed a light on the nature of the changes occurring during the course of the conversion of substrates into products. It turned out that in the decomposition process of both 1a and 1b, there is only one transition state (Figure 1) between the energy minima of substrate and product. Any attempt to find an alternative reaction pathway leading through a zwitterionic structure – also in a simulated presence of a polar medium – has failed.

Calculations B3LYP/6-31G(d) have shown that the elimination of sulfur dioxide molecule from the substrate requires overcoming a relatively large activation barrier. Surprisingly, it turned out that depending on the structural isomer of substrate, the process can be realized with substantially different rates. In particular, the energy barrier of desulfonylation of Z-2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxide (1a) in the gas phase is higher than 12 kcal/mol in the analogous process involving E-2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxide (1b). A similar difference in reactivity of isomeric 2,5-dinitro-3,4-dimethyl-thiolene 1,1-dioxides has been shown by calculations in more advanced database functions: 6-31G(d,p), 6-31 + G(d), and 6-311G(d).

Comparison between the values of the entropies of activation leads to important conclusions. Change in ΔS values – regardless of substrate isomerism and the polarity of the medium – does
not exceed generally 3 cal/mol K. It is typical for the reactions proceeding through highly organized transition states.\textsuperscript{12}

Finally, a detailed analysis of IRC trajectory (Figure 1) indicates that the reactions must not be included into a group of "one-step, two-stage"\textsuperscript{13,14} processes. This suggests that the disintegration of C-S bonds should be characterized by a very similar degree of advancement (see also next section).

**Key structures**

Analysis of reaction energy profiles showed that during the decomposition of both 1\textsubscript{a} and 1\textsubscript{b}, between the energy minima of the substrate and the product, there is only one transition state (TS). As demonstrated by B3LYP/6-31G(d) simulation, transition state structures have similar five-membered ring structures (Figure 2 and Table 2). Within each of these, takes place an sp\textsuperscript{3}→sp\textsuperscript{2} rehybridization in the reaction centers C2 and C5. This is accompanied by the disintegration of S1-C2 and C5-S1 bonds. At the same time, the C3-C4 bond is losing its double bond character, and the C2-C3 and C4-C5 bonds start to gain double bond character. The disintegration of S1-C2 and C5-S1 bonds is being carried out simultaneously and with a high synchronicity.

Therefore, the transition states of the studied reactions can be structurally correlated with the transition states of retro-[4+1] cycloaddition reactions. In accordance with the principle of microscopic reversibility of reactions, a hypothetical [1+4] cycloaddition of sulfur dioxide to dienes 2\textsubscript{a} and 2\textsubscript{b} should be proceeding by identical transition states as it was in the case of processes 1\textsubscript{a}→2\textsubscript{a}+SO\textsubscript{2} and 1\textsubscript{b}→2\textsubscript{b}+SO\textsubscript{2} respectively. Due to a significant difference in global electrophilicity and electronic chemical potentials of diene (\(\omega = 2.80 \text{ eV}, \mu = -0.1960 \text{ a.u. for } 2\text{a} \), and \(\omega = 2.92 \text{ eV}, \mu = -0.1979 \text{ a.u. for } 2\text{b} \)) and sulfur dioxide (\(\omega = 3.70 \text{ eV}, \mu = -0.2316 \text{ a.u.} \)), one would expect that transition states will have a polar character, which is caused by a non-uniform redistribution of electron density. Such a phenomenon is observed in the case of polar cycloaddition – with or without participation of symmetrically substituted addition products, e.g., cyclopentadiene or tetracyanoethene (GEDT is even 0.43e).\textsuperscript{13} Origin of this phenomenon has been discussed recently in detail.\textsuperscript{13} Meanwhile, surprisingly it was found that transition states exhibit very low polar character (GEDT < 0.10e). In next step, we have re-optimized both transition states using UB3LYP/6-31G(d) theory level. It was found that both transition states have a non-biradicaloid character (\(<S2>\) values, which in both cases equal to 0.00).
Calculations in more advanced basis sets 6-31G(d,p), 6-31+G(d), or 6-311G(d) provide a very similar picture of transition states.

An increase in the polarity of the reaction medium makes S1–C2 and C5–S1 bonds to disintegrate slowly. However, this applies to, in a comparable extent, both C–S principal bonds. Their polarity does not change significantly with the introduction of polar medium. This is evidenced by the values of Global Electron Density Transfer (GEDT) indices.

### Computational methodology

The quantum-chemical calculations were performed using hybrid B3LYP functional and 6-31G(d) included in the Gaussian 09 package.\textsuperscript{15} Reports published recently show that simulations using the PCM model suggest that the impact of environment polarity on the reaction should be minimal.

Optimization of stable structures was performed with the Berny algorithm, whereas the transition states were calculated using the QST2 procedure followed by the transition state method. Stationary points were characterized by frequency calculations. All reactants and products had positive Hessian matrices. All transition states showed only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. For all reactions, IRC calculations were performed to connect previously computed transition structures with suitable minima.

Global electron density transfer\textsuperscript{18} was calculated according to the following formula:

\[
\text{GEDT} = - \sum q_A,
\]

where \(q_A\) is the net charge, and the sum is taken over all the atoms of dipolarophile.

Global electronic properties of products were estimated according to the equations recommended by Parr and Yang\textsuperscript{19} and Pérez et al.\textsuperscript{20} In particular, the electronic chemical potential (\(\mu\)) and chemical hardness (\(\eta\)) were evaluated in terms of one-electron energies of FMO \((E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\) using the following equations:

\[
\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2,
\]

\[
\eta = E_{\text{LUMO}} - E_{\text{HOMO}}.
\]

Next, the values of \(\mu\) and \(\eta\) were used for the calculation of global electrophilicity (\(\omega\)) according to Formula (4):

\[
\omega = \mu^2 / 2\eta
\]

### Conclusions

It has been shown by quantum-chemical calculations that the process of thermal decomposition of 2,5-dinitro-3,4-dimethyl-thioline 1,1-dioxides is proceeding by one-step mechanism through the transition states of high symmetry and, unexpectedly, of low polarity. The reaction mechanism can be equated to the process of retro-[4+1]-cycloaddition. Simulations using the PCM model suggest that the impact of environment polarity on the reaction should be minimal.

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