



Quantum chemistry and TST study of the mechanism and kinetics of the butadiene and isoprene reactions with mercapto radicals

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Abstract

The reactions of isoprene and butadiene with SH[•] radicals have been investigated by density functional theory and ab initio molecular orbital theories. We report the thermodynamics and kinetics of four different pathways, involving addition of SH[•] radicals to all double-bonded carbon atoms. Calculations have been performed on all stationary points using BHandHLYP functional, Moller–Plesset perturbation theory to second-order (MP2) and the composite CBS-QB3 method at the MP2 optimized geometries and frequencies. Pre-reactive complexes have been identified. The apparent activation energies are negative for SH[•] addition at the terminal carbon atoms and are slightly smaller than those for OH[•] addition at the same positions. The calculated overall rate coefficient for butadiene + SH[•] reaction at 298 K is in excellent agreement with the only available experimentally measured value. Activation energies and overall rate coefficients at different temperatures are predicted for the first time for butadiene + SH[•] and isoprene + SH[•] reactions. The reactions of butadiene and isoprene with SH[•] radicals were found to be about four times faster than with OH[•] radicals.

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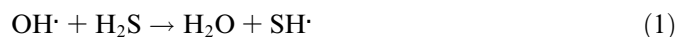
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1. Introduction

Hydrogen sulfide (H₂S) is emitted by natural sources, such as the decomposition of organic marsh matter and volcanic activity, and anthropogenic sources, like the man-made pollution due to burning of sulfur containing fossil fuels [1]. The average life-time of hydrogen sulfide in the atmosphere is a few hours. It is the main source of mercapto radicals (SH[•]) [2], which is the simplest sulfur molecular compound. It has been suggested that this radical could be very abundant in oxygen rich giant star atmospheres [3]. The first astronomical detection of SH[•] was recently reported by Yamamura et al. who identified its ro-vibrational lines in the infrared spectrum [4] in the

S-type star R-Andromedae. It has been found in the solar photosphere by Berdyugina et al. using high resolution UV [5].

The SH[•] radical is thought to be formed in the atmosphere by the reaction of hydrogen sulfide with OH[•] radicals. This is probably the major loss mechanism for H₂S:



Also it has been identified as a minor product of the reactions of OH[•] with CS₂, OCS and the NO₃ radical with H₂O [6], although these reactions are slow and probably do not constitute important sources of SH[•] radicals in the atmosphere. In the laboratory, SH[•] is obtained from the reactions of F[•], H[•] and OH[•] with hydrogen sulfide, or by photolysis of H₂S. In the troposphere the hydrogen sulfide conversion to SH[•] competes with its oxidation to sulfur oxides (SO_x), and the latter is the predominant route. However, it is conceivable that in a slightly oxidizing

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environment such as remote places on the surface of the sea, near marshes, volcanic areas and water treatment plants, the mercapto radical could be in high enough concentrations for its reactivity to be significant. In the stratosphere and in some extraterrestrial atmospheres, SH[•] radicals have been detected in concentrations that are much larger than in the troposphere [6,7].

On the other hand, isoprene and butadiene are emitted in very large quantities. The former is produced mainly by plants, but also by human activities, while the latter is of anthropogenic origin [8]. Because of their reactivity with hydroxyl radicals, with ozone and with NO₃, they play an important role in the photochemistry of both urban and rural areas therefore.

Only a few experimental data are available for the reactions of volatile organic compounds with mercapto radicals [9]. They indicate, however, that reaction with SH[•] might be even faster than with OH[•] radicals. Experimental values have been reported for the reaction with selected alkenes and dienes. Estimates of the rate constant coefficients have been reported at 298 K for ethene [10] and 1-butene, propadiene, butadiene and 1,4-cyclohexadiene [11], and the temperature dependence of the ethene + SH[•] reaction has been determined in the range 296–455 K [12]. The temperature dependence of *k* for a similar reaction, the addition of a methyl thiyl radical (CH₃S[•]) to butadiene, has been studied in the range 296–333 K [12]. Its activation energy has been found to be negative and smaller than for the corresponding reaction with OH[•] (−0.60 kcal/mol for CH₃S[•] [12] and between −0.87 and −0.93 kcal/mol for OH[•] [9,13]).

No theoretical work on the SH[•] radical addition to double bonds has been published. In this work, quantum chemistry and computational kinetics calculations have been performed to determine the mechanism and rate constant coefficients of SH[•] addition to butadiene and isoprene. Pre-reactive complexes have been identified in all cases. Rate constants have been obtained using transition state theory. The theoretical value for butadiene at 298 K is compared with the experimental data reported by Perner and Franken [11], and used to validate the methodology. Activation energies and overall rate constant coefficients at different temperatures are predicted for the first time for the butadiene + SH[•] and isoprene + SH[•] reactions.

2. Computational methodology

Electronic structure calculations have been performed with the system of programs Gaussian98 [14]. Unrestricted ab initio methods have been used to calculate the energies of the radicals. Two different approaches are used to optimize the geometries: density functional methods (DFT) and Moller–Plesset perturbation theory. The reason for using both of these methods simultaneously is that they have often been found to be complementary [13,15,16]. Optimized geometries are sometimes more easily obtained with either one of the two methods, although no clear explanation for this has been advanced. For transition

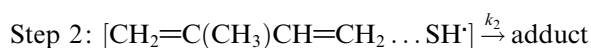
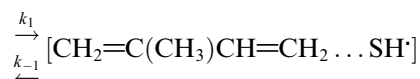
states, there have been reports that DFT is not always adequate or reliable while, for potential energy minima, it is often efficient and fast. However, in many computational chemistry calculations we have obtained excellent agreement with experimental data using the BHandHLYP method [13,15]. In MP2, and especially in other highly correlated calculations such as QCISD(T) and CCSD(T), the problem of spin contamination may be a drawback. It has been previously reported that highly correlated methods overestimate reaction barriers in OH[•] addition reactions to double bonds [17]. In addition, and to avoid the problem of the basis set superposition error and to minimize the basis set truncation error, the energy profiles were recalculated using the complete basis set extrapolation CBS-QB3 approach [18] at the previously optimized MP2/6-311++G(d,p) geometries and using the corresponding frequencies. The MP2 geometries were chosen instead of the default B3LYP geometries because the latter method often does not yield adequate transition state geometries or the adiabatic transition states cannot be located, see for example [19]. In other cases, it has been possible to identify the variational transition state but the adiabatic transition state does not exist on the potential energy surface, see for example [20]. Another important feature of the CBS-QB3 methodology is that it also corrects for spin contamination (proportional to $\langle S^2 \rangle$).

Single point selected calculations are also performed with the MP2 method using larger basis sets. In Dunning's correlation consistent triple zeta basis set [21,22], the cc-pVTZ, 4s, 3p, 2d and 1f valence polarization functions are used to represent the carbon and sulfur atomic orbitals, while 3s, 2p and 1d functions are used for hydrogen.

Geometries are fully optimized at the BHandHLYP/6-311G(d,p), MP2/6-311G(d,p) and MP2/6-311++G(d,p) levels and the character of the stationary points is confirmed by frequency calculations performed at the same levels. All the reported transition states present one, and only one imaginary frequency corresponding to the expected transition vector. In addition, intrinsic reaction coordinate calculations (IRC) [23] have been carried out to verify that the transition states connect reactants and products.

All energy differences have been corrected for the zero point vibrational frequencies (ZPE) using unscaled frequencies. Thermal corrections (TCE) are used for reaction enthalpies. In the case of perturbation theory calculations, projected energies (PMP2) are used throughout.

As in previous work on the addition of OH[•] to double bonds [13,15], we assume that the SH[•] + dienes initial reaction occurs according to the following two-step mechanism:



In the first step, a fast thermal equilibrium is established between the reactants and a loosely bound pre-reactive complex. The second step is the irreversible formation of the adduct. The existence of a pre-reactive complex that is formed without activation energy is necessary to explain the existence of a negative activation energy [13,15,24]. This mechanism was first proposed by Singleton and Cvetanovic [25]. It just means that the pre-reactive complex is more stable than the isolated reactants in terms of enthalpy, although not in terms of free energy. To use the steady state approximation as proposed by Singleton and Cvetanovic, it is necessary that the sum of k_2 and k_{-1} be larger than k_1 . Since $k_{-1} \gg k_2$, it means that $k_{-1} > k_1$ i.e. it is necessary to assume that the pre-reactive complex is less stable, in terms of Gibbs free energy, than the isolated reactants. The rate constant equation may then be written as

$$k = \frac{k_1 k_2}{k_{-1}} = \left(\frac{A_1 A_2}{A_{-1}} \right) e^{-(E_1 + E_2 - E_{-1})/RT} \quad (2)$$

Since E_1 is equal to zero, the apparent activation energy is

$$\begin{aligned} E_{\text{app}} &= E_2 - E_{-1} = (E_{\text{TS}} - E_{\text{RC}}) - (E_{\text{R}} - E_{\text{RC}}) \\ &= E_{\text{TS}} - E_{\text{R}} \end{aligned} \quad (3)$$

Thus, in this approximation, E_{RC} cancels out, and the pre-reactive complex is not included in the final rate coefficient equation.

The apparent activation energy of the reaction can be calculated by using only the energies of the transition states and of the reactants, and the rate coefficient for the overall reaction becomes

$$k = K_{\text{eq}} \cdot k_2 = \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{R}}} e^{-(E_{\text{TS}} - E_{\text{R}})/RT} = A e^{-E_a/RT} \quad (4)$$

where K_{eq} is the equilibrium constant of Step 1, the Q 's are the partition functions of the transition state and of the reactants, and the energy barrier is obtained according to the following equation:

$$E_a = E_{\text{TS}} - E_{\text{R}} + \text{ZPE}_{\text{TS}} - \text{ZPE}_{\text{R}} \quad (5)$$

For reaction energies at 298 K, thermal corrections (TCE) are applied. Entropy changes have also been calculated at 298 K.

Canonical transition state theory (CTST), as implemented in the Rate 1.1 program [26], has been used to calculate the reaction rate constants for the formation of the adducts. As usual, the vibrational partition functions are corrected, when needed, by replacing some of the low frequency vibrations by the corresponding hindered internal rotations. Arrhenius pre-exponential factors are determined. The calculated rate coefficients are high pressure limit rate coefficients. There are no data on the pressure dependence of this reaction. However, it is known that the reaction of isoprene and butadiene with OH^\bullet radicals is pressure independent between 60 and 600 Torr [27]. By analogy, it seems safe to assume that the reaction with

SH^\bullet radicals at atmospheric pressure is also pressure independent.

3. Results

In its most stable conformation, the carbon chain in isoprene and butadiene is *trans*. The SH^\bullet radical attack on dienes is, as expected, very similar to the one observed in the reaction of dienes with OH^\bullet radicals [13,15]. At first, a stable vdW complex is formed between the SH^\bullet radical and the diene. When basis set without diffuse functions are used, a vdW complex is formed through the interaction between the partially positive charged hydrogen atom in the polar SH^\bullet radical and any one of the double bonds in the diene. However, when the basis is increased to 6-311++G(d,p), the geometries of the complexes change and the role of the London dispersion forces between S atom and the rich electron density π bond become more important. One pre-reactive complex (PR) is identified in the case of the butadiene + SH^\bullet reaction, while two different complexes (PR_{1-2} and PR_{3-4}) were found for isoprene (Figs. 1 and 2). Their structures are stabilized by the vdW attraction between the π electron density on the double bond and the SH^\bullet radical, mainly involving the S atom. The pre-reactive complexes of isoprene are more stable than that of butadiene because of the inductive effect of the methyl group that increases the electron density in double bonds, and also because of the possibility of long range attractions between the sulfur atom and the methyl hydrogen atoms. The MP2/6-311++G(d,p) pre-reactive complex structures are represented in Figs. 1 and 2 and their stabilization energies, relative to the energy of the isolated reactants and including ZPE corrections, are reported on the figures. The stabilization energies for the two pre-reactive complexes of isoprene are practically the same.

The structures of the complexes, obtained at BHandH-LYP/6-311G(d,p) and MP26-311G(d,p) levels of theory are similar to those previously obtained for OH -dienes systems [13,15] i.e. similar to non-conventional hydrogen bonds between positive charged hydrogen atoms and double bonds.

Comparing the stabilization of the pre-reactive complexes of dienes with SH^\bullet and OH^\bullet radicals [13,15], it is

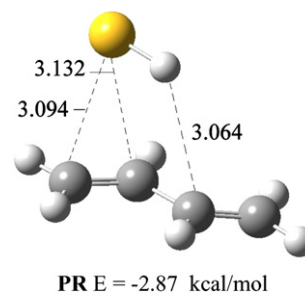


Fig. 1. MP2/6-311++G(d,p) optimized structure of the pre-reactive complex of butadiene + SH^\bullet (bond distances in Å). Energy relative to separated reactants.

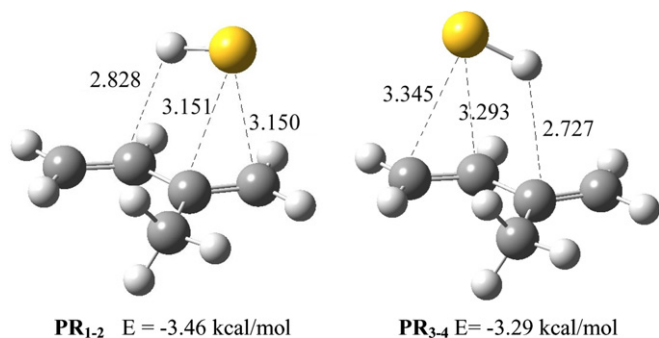


Fig. 2. MP2/6-311++G(d,p) optimized structure and energies, relative to separated reactants, of the pre-reactive complexes of isoprene + SH \cdot (bond distances in Å).

observed that independently of the different structures, the stabilization energies are very similar. The energies of the pre-reactive complexes of OH \cdot with butadiene and isoprene are more than 3 kcal/mol lower than those of the isolated reactants, i.e. similar in values to those involving SH \cdot (Fig. 2). This can be explained by the compensation of the OH \cdot ability to form unconventional H bonds involving π electrons [13,15,24] with the ability of sulfur atom to form relatively strong vdW complexes.

From the pre-reactive structures, the SH \cdot radical approaches one of the carbon atoms, as the energy increases to a maximum at the transition state. The MP2 optimum geometries of the transition states of butadiene and isoprene with SH \cdot radicals are represented in Figs. 3 and 4. Relevant parameters have been indicated on the figures. The SH radical lies in a plane approximately parallel to the plane of the carbon chain, with the sulfur atom directly above the carbon atom to which it will attach. The hydrogen atom of SH \cdot lies in the direction of the double bond. The S \cdots C distances are about 2.4 Å for the internal carbon atoms, and slightly longer (2.5 Å) for the external carbons. Because the transition states occur early, most of the C=C double bond character is retained. The almost planar geometry of the bonds around the carbon atom is also an indication of an early transition state. The results are very similar to the ones obtained for addition of OH \cdot to butadiene and isoprene [13,15].

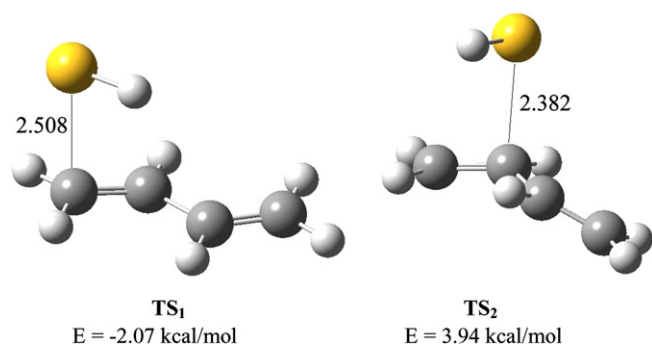


Fig. 3. MP2/6-311++G(d,p) optimized structures and energies, relative to separated reactants, of the transition states (bond distances in Å) for butadiene.

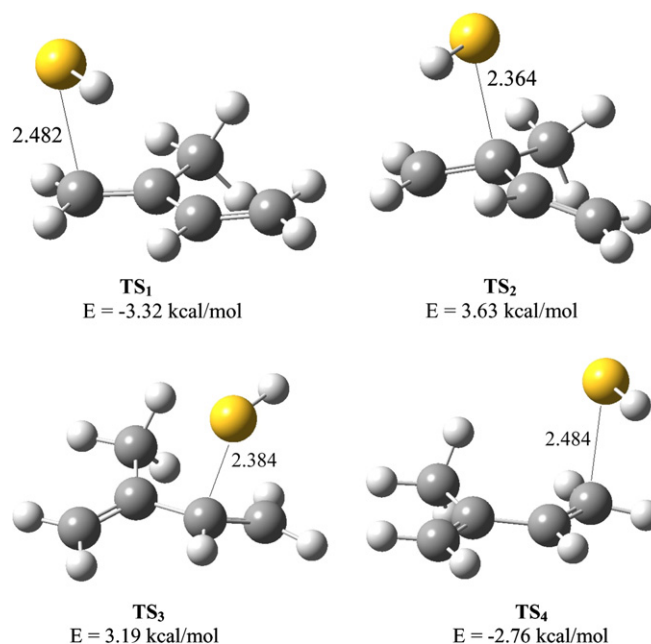


Fig. 4. MP2/6-311++G(d,p) optimized structures of the transition states (bond distances in Å) for isoprene. Energies relative to separated reactants.

The transition vectors clearly correspond to the expected motion of the sulfur atom approaching one of the carbons. The BHandHLYP imaginary frequencies are noticeably smaller than those obtained with the MP2 method. With both methods, however, the highest frequencies correspond to addition to internal carbon atoms, indicating tighter transition states (Table 1).

To verify that the transition states indeed connect the products and pre-reactive complexes, an IRC calculation was performed for addition of SH \cdot to an external carbon atom of butadiene (TS1) using the MP2 method.

The reaction barriers, calculated as the energy difference between transition states and the isolated reactants, including ZPE corrections, are reported in Table 2 for the SH \cdot addition to all positions in butadiene and isoprene. The difference between the addition barriers at internal and

Table 1

Unscaled imaginary frequencies, in cm^{-1} , at the transition states in the SH \cdot addition to butadiene and isoprene internal and external carbon atoms

	MP2/ 6-311G(d,p) ν_i (cm^{-1})	MP2/ 6-311G++(d,p) ν_i (cm^{-1})	BHandHLYP/ 6-311G(d,p) ν_i (cm^{-1})
<i>Butadiene</i>			
C ₁	340i	339i	47i
C ₂	458i	444i	363i
<i>Isoprene</i>			
C ₁	350i	355i	118i
C ₂	477i	464i	362i
C ₃	437i	432i	365i
C ₄	358i	370i	79i

Table 2

Activation energies, in kcal/mol, for addition of SH[•] to carbons atoms of butadiene and isoprene

	PMP2/6-311G(d,p)	PMP2/cc-pVTZ//MP2/6-311G(d,p)	BHandHLYP/6-311G(d,p)	CBS-QB3//MP2/6-31++G(d,p)
<i>Butadiene</i>				
C ₁	0.6	−0.86	−1.5	−2.04
C ₂	6.8	–	5.5	3.94
<i>Isoprene</i>				
C ₁	−0.45	−1.59	−1.2	−3.32
C ₂	6.3	–	6.6	3.63
C ₃	5.7	–	5.0	3.19
C ₄	0.05	−0.97	−1.7	−2.76

external carbons is of about 6–7 kcal/mol for both dienes, independently of the calculation method. This difference is even larger than that corresponding to the OH[•] reaction paths [13,15], and the addition to internal carbon atoms is therefore expected to be negligible.

It is important to notice that the MP2/cc-pVTZ, BHandHLYP/6-311(d,p) and CBS-QB3//MP2 methods yield negative activation energies for additions at external carbons. The values obtained here are slightly lower than those obtained with the same methods for the reaction of OH[•] with dienes, in qualitative agreement with the fact that the experimental rate constant at 298 K of the reaction with SH[•] is 1.5 times larger than with OH. A discrepancy is observed between the results obtained with the different employed methods, with regard to the preference for addition of SH[•] at the C₁ and C₄ carbon atoms in isoprene. While the MP2 method favors C₁, the DFT method favors C₄. The CBS-QB3 results favor addition to C₁ by 0.56 kcal/mol, in agreement with the expected structure–reactivity relationship.

The reaction energies for the SH[•] + butadiene and isoprene reactions at 298 K, in kcal/mol and corrected for the TCE, are given in Table 3 for all methods and for all addition channels. No experimental results are available for comparison. Again, the methods used yield different absolute values but similar relative results. Addition at the internal carbon atoms yields adducts that are about 15–18 kcal/mol less stable than the ones obtained by addition at external carbons (as compared to approximately

Table 3

Reaction energies at 298 K, in kcal/mol, for addition of SH[•] to butadiene and isoprene

	PMP2/6-311G(d,p)	PMP2/cc-pVTZ	BHandHLYP/6-311G(d,p)	CBS-QB3//MP2/6-31++G(d,p)
<i>Butadiene</i>				
C ₁	−21.0	−20.9	−18.6	−19.19
C ₂	−3.0	–	0.14	−2.51
<i>Isoprene</i>				
C ₁	−20.2	−20.0	−17.4	−19.91
C ₂	−2.1	–	1.4	−3.75
C ₃	−1.33	–	0.38	−2.57
C ₄	−19.3	−18.9	−16.4	−18.02

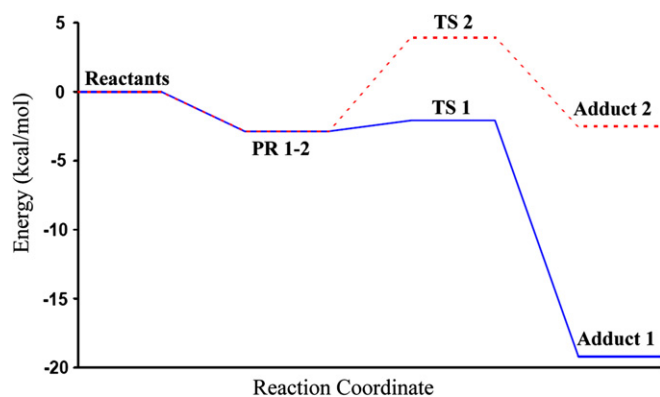


Fig. 5. CBS-QB3//MP2 energy profiles for SH[•] addition to external (path 1) and internal (path 2) carbon atoms in butadiene.

15 kcal/mol for OH[•]). Addition at C₁ is consistently favored, although adducts with the SH group at C₄ are almost as stable as the ones at C₁. This is quite different than what is observed for the OH adducts and suggests that, for the SH[•] reactions, additions at both ends of isoprene lead to adducts that are close in energy. The stability of the SH[•] adducts is approximately half the one of the corresponding OH[•] adducts, in agreement with the smaller electronegativity of the sulfur atom and its greater size.

The energy profiles obtained using the CBS-QB3//MP2 energies for butadiene + SH[•] are shown in Fig. 5. The formation of a pre-reactive complex followed by a transition state lower in energy than the isolated reactants is clearly observed for the paths involving addition to the external carbon atoms.

4. Rate coefficient calculations

The butadiene and isoprene reaction with SH[•] radicals involves several pathways, with different transition structures leading to various products. To simplify the analysis we assume that, once the system is engaged in a specific pathway, it proceeds independently of the other pathways and no mixing or crossover occurs. Thus, the overall rate constant, which measures the rate of SH[•] disappearance, is determined as the sum of the rate coefficients calculated for the different pathways. However, rate coefficients corresponding to additions to C₂ and C₃ (C₂ in butadiene) have not been included because they are so much smaller (4–6 orders of magnitude, depending on level of theory and reactant), than those of channels 1 and 4 (channel 1 in butadiene) that their contributions are negligible.

The only available experimental result for the reactions studied in this work is the rate coefficient, at 298 K, for butadiene + SH[•]. Thus, this value is used to validate the methodology. The rate coefficient is calculated using Eq. (3). As explained in the methodology section, internal rotations with barriers smaller than 2.5 kcal/mol have to be identified and treated as rotations in the calculation of the partition functions. In the dienes + SH[•] transition state, only one such internal rotation occurs in each transition

state. It corresponds to the rotation of the SH \cdot hydrogen atom around the C \cdots S axis, as shown in Fig. 6.

Plots of the electronic energy as a function of the C–C–S–H dihedral angle, obtained using both the MP2/6-311(d,p) and BHandHLYP/6-311(d,p) methods, present maximum barriers of 1.9 and 1.3 kcal/mol, respectively. Thus, this motion has to be treated as a rotation in the calculation of the transition state partition function. In the case of the reaction of butadiene with OH \cdot this correction was not necessary because the corresponding barriers were found to be 5.6 and 4.3 kcal/mol, respectively. The OH \cdot hydrogen atom is closer to the hydrogen atoms of butadiene and the repulsion is greater, which explains that the barrier to rotation is larger than in the case of SH \cdot . The hindered rotor approximation has been used to correct the Q_s corresponding to these internal rotations. The modes corresponding to hindered rotations were identified by direct inspection from frequency calculations using the GaussView tool. Then, these modes were removed from the vibrational partition function of the corresponding specie and replaced with the hindered rotor partition function

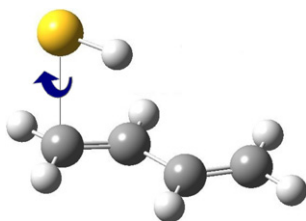


Fig. 6. Internal rotation around the CS axis in the butadiene + SH \cdot transition state.

Table 4
Overall rate coefficient $\times 10^{11}$, in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for SH \cdot addition to external carbons in butadiene

T (K)	MP2/6-311G(d,p)	BHandHLYP/6-311G(d,p)	CBS-QB3//MP2/6-31++G(d,p)	Experimental [11]
250	1.14	8.21	20.4	–
298.15	1.09	6.00	11.1	9.96
300	1.08	5.94	10.9	–
400	1.01	4.31	7.20	–
450	0.99	4.02	5.40	–
500	0.99	3.87	4.41	–

Bold values represent the most important values.

Table 5
Rate coefficients $\times 10^{11}$, in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for SH \cdot addition to external carbon atoms in isoprene

T (K)	BHandHLYP/6-311G(d,p)		CBS-QB3//MP2/6-31++G(d,p)		BHandHLYP/6-311G(d,p)	CBS-QB3//MP2/6-31++G(d,p)
	k_1	k_4	k_1	k_4	k_{overall}	k_{overall}
250	4.88	3.75	53.9	17.6	8.39	71.42
298.15	4.27	2.45	19.7	7.71	6.72	27.41
300	4.25	2.42	19.1	7.51	6.68	26.60
400	3.91	1.65	9.4	4.23	5.57	13.61
450	3.95	1.51	5.6	2.82	5.46	8.464
500	4.07	1.43	3.9	2.11	5.50	5.984

Bold values represent the most important values.

(Q^{HR}). In our calculations we have adopted the analytical approximation to Q^{HR} for a one-dimensional hindered internal rotation proposed by Ayala and Schlegel [28].

The calculated rate coefficients of the butadiene + SH \cdot reaction are shown in Table 4. The best agreement with the experimental value at 298 K was obtained at CBS-QB3//MP2/6-31++G(d,p), at this level the calculated rate constant was found to be only 1.1 times higher than the experimental one. It is interesting to notice that the BHandHLYP/6-311G(d,p) result is also in excellent agreement with the experimental value at a significantly lower computational cost, in this case the calculated value is underestimate by a factor of 1.6. However at low temperatures the discrepancies are larger, we assume that CBS results are more accurate, but only experimental determination of Arrhenius parameters would elucidate that point. The largest discrepancy was found at MP2/6-311G(d,p), with the calculated rate coefficient about nine times lower than the experimental one.

Once BHandHLYP and CBS-QB3//MP2 were defined as the most appropriate methods, calculations were performed, using these methods, for the analogous isoprene + SH \cdot reaction. In this case, the methyl internal rotation may have to be considered. Although it occurs in both isoprene and the isoprene–SH \cdot transition state, the corresponding contribution to the partition functions could be too different to cancel in Eq. (3). Hence, the barrier to methyl rotation was calculated in the transition state, and it was determined that it is very small, 0.4 kcal/mol, and similar to the one for free isoprene. Thus, its contribution to the partition functions of the transition state and of isoprene cancels and it is not necessary to replace it in the calculation of k . At 298 K, the rate constant of isoprene + SH \cdot is predicted to be $2.74 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, at the highest level of theory, i.e. 2.47 times greater than the value for the butadiene + SH \cdot reaction. The calculated rate constants for the isoprene + SH \cdot reaction are shown in Table 5. For comparison, the calculated rate coefficients at 298 K for addition of OH \cdot and SH \cdot at the external carbons of butadiene and isoprene are reported in Table 6.

It is interesting to notice that the rate coefficients of isoprene and butadiene calculated with the CBS-QB3//MP2 method are larger than those obtained with BHandHLYP and MP2. The ZPE corrected activation energies (Table 2) are higher when calculated using BHandHLYP and MP2

than at the CBS-QB3//MP2 level. This is in contradiction with the assumption that the BSSE affects “low” level calculations. If that were the case the CBS method should give larger activation energies and lower rate coefficients. The reason for this “unexpected” result was pointed out by Dunning: “It is quite possible and even probable that the binding energies computed without the counterpoise correction, are closer to the complete basis set limit than the corrected values. This frustrating (or lucky) situation (depending on your proclivities) is due to the fact that the BSSE and the basis set convergence error are often of opposite signs” [29]. CBS-QB3 corrects both kinds of errors, while the counterpoise approach, using relatively small basis set, corrects only the first one, leading to artificially high energies. In other words even when the BSSE is an unquestionable error in low level calculations it usually compensates with other errors such as basis set incompleteness error. This was shown in a recent article for the H abstraction by Cl from formaldehyde [30]. Therefore the only way to get reliable, and BSSE free, energies is to extrapolate to complete basis set. To clarify this we have calculated the BSSE for the transition states for the attack

Table 6
Comparison of partial rate constants $\times 10^{11}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 298.15 K

	k_{OH} Ref. [15]	$k_{\text{SH(CBS-QB3)}}$
<i>Butadiene</i>		
C ₁	1.26	5.51
<i>Isoprene</i>		
C ₁	4.73	19.7
C ₄	2.13	7.71

of SH^\bullet to C₁ and C₄ of isoprene at PMP2/6-311++G(d,p) using the conventional two fragments approach. The values of the ZPE corrected energy barriers without CP correction are -3.68 kcal/mol and -2.46 kcal/mol , respectively, which are in quite good agreement with the CBS-QB3 values. However the corresponding BSSE corrections are 5.13 kcal/mol and 4.73 kcal/mol which rise the barriers to 1.45 and 2.27 kcal/mol , respectively, leading to large disagreements with the CBS-QB3 values. For most systems of chemical interest the CBS extrapolation is computationally unaffordable. Fortunately this is not the case for the quantum chemical treatment of the particular systems treated in this work. Nevertheless it seems that at “low” level calculations a cancellation of errors of opposite signs occurs, which according to Refs. [29,30] and to our present results, is systematic rather than fortuitous.

Arrhenius plots of partial and overall butadiene and isoprene rate constants are shown in Fig. 7. Both exhibit a weak temperature dependence, as well as negative activation energies characteristic of many radical addition reactions to double bonds. Overall Arrhenius expressions for the rate coefficients can be expressed as $k_{\text{overall BHAndHLYP}}(\text{butadiene}) = 1.5 \times 10^{-11} e^{0.86/RT}$; $k_{\text{overall CBS//MP2}}(\text{butadiene}) = 6.82 \times 10^{-12} e^{1.66/RT}$ and $k_{\text{overall}}(\text{isoprene}) = 2.91 \times 10^{-11} e^{0.54/RT}$; $k_{\text{overall CBS//MP2}}(\text{isoprene}) = 2.84 \times 10^{-12} e^{2.72/RT}$.

5. Conclusions

In this work, the rate constants of butadiene and isoprene with the SH^\bullet radical have been calculated. Only the addition to external carbons is significant. The value of the rate constant obtained for the butadiene reaction + SH^\bullet

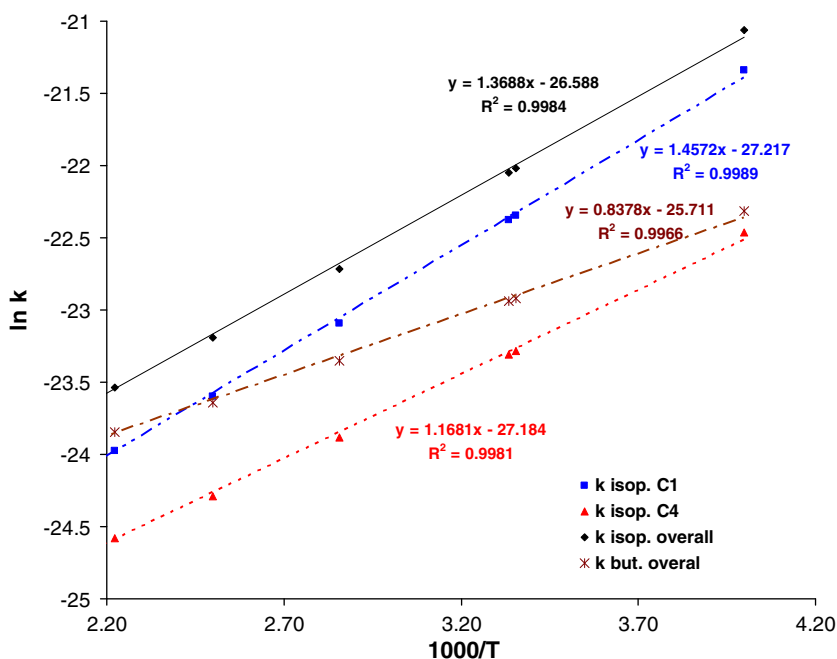


Fig. 7. Arrhenius plots for the calculated overall and partial isoprene and butadiene + SH^\bullet reactions at the CBS-QB3//MP2 level of calculations.

agrees very well with the only reported experimental value, which corresponds to the constant at 298 K. The value calculated for isoprene is predicted here for the first time. Rate constants are obtained at different temperatures, and activation energies are proposed for the first time. The negative activation energies characteristic of many radical additions to double bonds are obtained. The calculated results predict that reaction with SH^\bullet is about four times faster than with OH^\bullet , thus implying that it might have atmospheric consequences in areas in which the H_2S concentration is large. Experimental measurements of the temperature dependence of both reactions are desirable. They would prove if the predictions from this work are accurate or not and which calculated rate coefficients are more accurate.

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References

- [1] P. Brimblecombe, Biogeochemical cycles, Encyclopedia of Atmospheric Sciences, Elsevier Science Ltd., 2003.
- [2] A.G. Császár, M.L. Leininger, A. Burcat, *J. Phys. Chem. A* 107 (2003) 2061.
- [3] T. Tsuji, *Astron. Astrophys.* 23 (1973) 411.
- [4] I. Yamamura, K. Kawaguchi, S.T. Ridgway, *Astrophys. J.* 528 (2000) L33.
- [5] S.V. Berdyugina, W.C. Livingston, *Astron. Astrophys.* 387 (2002) L9.
- [6] G.S. Tyndall, A.R. Ravishankara, *Int. J. Chem. Kinet.* 23 (1991) 483.
- [7] S.M. Resende, F.R. Ornellas, *J. Phys. Chem. A* 104 (2000) 11934.
- [8] Stefan Reimann, Pierluigi Calanca, Peter Hofer, *Atmos. Environ.* 34 (2000) 109.
- [9] The NIST Chemical Kinetics Database, NIST Standard Reference Database; US Department of Commerce, Technology Administration, National Institute of Standards and Technology, Gaithersburg, MD, 17-2Q98.
- [10] N.L. Arthur, T.N. Bell, *J. Chem. Soc. [London]* (1962) 4866.
- [11] V.D. Perner, T. Franken, *Ber. Bunsen. Phys. Chem.* 73 (1969) 897.
- [12] R.J. Balla, B.R. Weiner, H.H. Nelson, *J. Am. Chem. Soc.* 109 (1987) 4804.
- [13] M. Francisco-Márquez, J.R. Alvarez-Idaboy, A. Galano, A. Vivier-Bunge, *Phys. Chem. Chem. Phys.* 5 (2003) 1392.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.3, Gaussian Inc., Pittsburgh, PA, 1998.
- [15] M. Francisco-Marquez, J.R. Alvarez-Idaboy, A. Galano, A. Vivier-Bunge, *Phys. Chem. Chem. Phys.* 6 (2004) 2237.
- [16] G. Bravo-Pérez, J.R. Alvarez-Idaboy, A. Galano, A. Cruz-Torres, *Chem. Phys.* 310 (2005) 213.
- [17] I.V. Tokmakov, M.C. Lin, *J. Phys. Chem. A* 106 (2002) 11309.
- [18] J.A. Montgomery Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, *J. Chem. Phys.* 110 (1999) 2822.
- [19] J.A. Beukes, B. D'Anna, V. Bakken, C.J. Nielsen, *Phys. Chem. Chem. Phys.* 2 (2000) 4049.
- [20] E.E. Greenwald, S.W. North, Y. Georgievskii, S.J. Klippenstein, *J. Phys. Chem. A* 111 (2007) 5582.
- [21] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [22] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [23] C. González, H.B. Schlegel, *J. Phys. Chem.* 94 (1990) 5523.
- [24] J.R. Alvarez-Idaboy, N. Mora-Diez, A. Vivier-Bunge, *J. Am. Chem. Soc.* 122 (2000) 3715.
- [25] D.L. Singleton, R.J. Cvetanovic, *J. Am. Chem. Soc.* 98 (1976) 6812.
- [26] W.T. Duncan, R.L. Bell, T.N. Truong, *J. Comp. Chem.* (1998) 1039.
- [27] P. Campuzano-Jost, M.B. Williams, L. D'Ottone, A.J. Hynes, *J. Phys. Chem. A* 108 (2004) 1537.
- [28] P.Y. Ayala, H.B. Schlegel, *J. Chem. Phys.* 108 (1998) 2314.
- [29] T.H. Dunning Jr., *J. Phys. Chem. A* 104 (2000) 9062.
- [30] M. Gruber-Stadler, M. Muhlhauser, S.R. Sellevag, C.J. Nielsen, *J. Phys. Chem. A* 112 (2008) 9.