



Computational investigation of thermal decomposition mechanism of 5-nitro-5-R-1,3-dioxane compounds

Pablo Ruiz^{1,2} · Silvia Quijano³ · Jairo Quijano¹

Received: 29 October 2021 / Accepted: 27 January 2022 / Published online: 30 March 2022
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract

This paper features the results of the computational study of thermal decomposition reaction of 5-nitro-5-R-1,3-dioxane compounds, with R = H, Br, and CH₃. Computational calculations were performed with M06-2X, MPWB1K, PBE0 and ω B97X-D functionals, and 6-311 + G(d,p) basis set in gas phase and also in solution with DMSO, at different temperatures. The kinetic and thermodynamic data obtained indicate a favoring of the reaction when the molecule presents substituent groups in position 5 and when carried out in DMSO, the stability of the molecules in their energetic components was discussed, too. For R = H two different reaction mechanisms were proposed and studied. Wiberg bond indices were obtained for the reactions studied and the results were examined in terms of bond formation and bond breaking progress as well.

Keywords Bronidox · DFT · Nitrous acid · Substituted dioxanes · Thermal decomposition · 5-Nitro-5-R-1,3-dioxanes

Introduction

Compounds of 1,3-dioxane type are involved in industrial processes as by-products, when used as solvents [1], or as reagents in synthesis processes in fine organic chemistry [2]. They have also been reported as biologically active compounds with anti-inflammatory properties, and effective modulators of multidrug resistance [3]. These compounds have also been considered for their enormous potential in terms of structural diversity, especially by substitution at positions 2 and 5 of the molecule [4, 5]. 1,3-Substituted molecules were found to display significant antifungal and antibacterial properties. Within this family of compounds, the most prominent have been the nitro and halonitro derivatives, especially because of their stability at a wider pH range (5–9). For instance, 5-bromo-5-nitro-1,3-dioxane (bronidox)

exhibits a broad spectrum of antimicrobial activity [5] and is an important reagent for ion-radical and oxide-reduction type reactions [2–6].

5-Bromo-5-nitro-1,3-dioxane is used as a preservative in rinses, cosmetics, and toiletries such as make-up, perfumes, toothpastes, soaps, shampoos, hand creams, and facial scrubs. [7].

Compounds derived from 1,3-dioxane can thermally decompose and release nitrous acid (HNO₂) or nitrogen oxides (NO_x) depending on the reaction mechanism [8, 9].

There is an experimental study of the thermal decomposition of 5-nitro-5-R-1,3-dioxane type compounds (Fig. 1 represents their general structure), in which the authors proposed a thermal decomposition mechanism for nitrous acid formation, similarly as represented in Fig. 2 [10].

Although there are computational studies on the formation of 1,3-dioxane compounds [11], we are not aware of published theoretical studies on their thermal decomposition.

The development of this project sought to computationally study the thermal decomposition of a series of 5-nitro-5-R-1,3-dioxane compounds at different temperatures. The findings obtained allowed to deepen in the reaction mechanism of their decomposition, to obtain the kinetic and thermodynamic parameters of the reaction as well as to correlate the activation energy with the structural characteristics of the molecules studied.

✉ Pablo Ruiz
paruizr@unal.edu.co

¹ Laboratorio de Fisicoquímica Orgánica, Facultad de Ciencias, Universidad Nacional de Colombia, Medellín 050034, Colombia

² Facultad de Ciencias Exactas Y Aplicadas, Instituto Tecnológico Metropolitano, Medellín, Colombia

³ Programa de Microbiología, Facultad de Ciencias Básicas, Universidad Santiago de Cali, Cali, Colombia

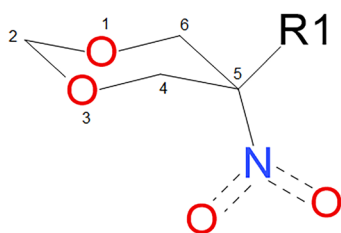


Fig. 1 Structure representation of 5-nitro-5-R-1,3-dioxane compounds

Methods

All calculations for this study were carried out in the Gaussian 09 computational package [12]. The geometrical parameters for all reactants, transition states, and products of the reaction studied were optimized using the density functional theory (DFT), with the functional M06-2X [13] and 6–311 + G(d,P) basis set [14]. (See Table S1 in supporting information). (Pre-calculations were performed on the molecules studied, but there were no significant differences in the results with larger basis set, see Table S2 in supporting information).

Vibrational frequency calculations at M06-2X [13], MPWB1K [15], PBE0 [16], and ω B97X-D [17] were conducted to obtain the kinetic and thermodynamic parameters of the reactions, which also allowed to characterize each structure as a minimum or saddle point within the potential energy surface. Scaling factors of 0.9658 and 0.9812 to M06-2X and PBE0, respectively, were used to correct the zero-point vibrational energy (ZPE), as previously recommended [18].

Computational calculations were accomplished at four different temperatures within the range of 503–563 K and 1 atm of pressure.

Enthalpy and entropy values were evaluated according to the standard thermodynamics equations [19]. Calculations in solution with dimethyl sulfoxide (DMSO) were achieved by the polarizable continuum model, using the integral equation formalism (IEFPCM) [20].

Calculations of the intrinsic reaction coordinate (IRC) [21] were performed on each of the localized transition state structures to verify that they connect to the corresponding stationary minimum points corresponding to the reactants and products. An example of IRC is shown in Fig. S1 in the supporting information.

The kinetic parameters were evaluated using classical transition state theory (TST), according to the Eyring–Polanyi equation [22, 23].

The population partitioning technique, natural bond orbital (NBO) [24, 25], has been used using the NBO program [26] implemented in the Gaussian 09 computational package [12]. Bond characteristics were obtained through Wiberg bond indices [27]. They are interpreted as a measure of bond order and bond strength among atoms. Processing these values generates additional indicators of both the bonds and the reaction. The percentage of evolution (%EV) is an indicator of the relative variation of the bond in the transition state, and has been calculated as:

$$\%EV = \delta\beta_i \times 100 \quad (1)$$

$\delta\beta_i$ relative variation of the Wiberg bond indices

where

$$\delta\beta_i = (\beta_i^{TS} - \beta_i^R) / (\beta_i^P - \beta_i^R) \quad (2)$$

β_i^{TS} , β_i^R , and β_i^P are the Wiberg bond indices corresponding to the bonds involved in the reaction center to transition state, reactant, and product, respectively.

Another important indicator calculated is the average relative variation [28]

$$\delta\beta_{av} = 1/n \sum \delta\beta_i \quad (3)$$

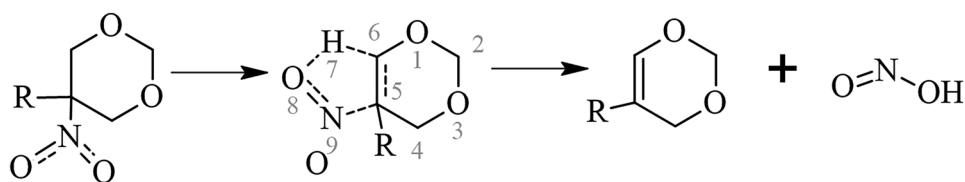
where n is the number of bonds to be considered in the reaction. The value obtained allows inferring characteristics of the transition state and is interpreted as a measure of the degree of progress of the transition state along the reaction coordinate.

The reaction is characterized by absolute synchronicity [28] (S_y), calculated from the Wiberg bond indices, according to the following expression:

$$S_y = 1 - \left[\frac{1}{(2n - 2)} \sum \frac{|\delta\beta_i - \delta\beta_{av}|}{\delta\beta_{av}} \right] \quad (4)$$

S_y is an indicator ranging from 0 to 1; high values for S_y imply that the reaction is highly synchronous.

Fig. 2 One-stage reaction mechanism of the thermal decomposition of 5-nitro-5-R-1,3-dioxanes, R = H, CH₃, Br



Results and discussion

Mechanism of the decomposition reaction

The thermal decomposition reaction of a series of 5-R-1,3-dioxane compounds with R = H, CH₃, and Br, was computationally modeled to observe the effect of the substituent group on the reaction parameters and mechanism.

The reactions were carried out under conditions simulating the gas phase and also in solution with DMSO as solvent. The mechanisms postulated in Figs. 2 and 3 were used as a starting point.

Figure 2 represents a reaction mechanism that proceeds through a 5-atom cyclic transition state and involves the breaking of the carbon–nitrogen bond and the migration of a hydrogen from carbon 6 to one of the oxygens of the nitro group, thus leading to the subsequent formation of the alkene: 5-R-4H-1,3-dioxine and a nitrous acid molecule.

Alternatively, when R = H, the two-stage mechanism depicted in Fig. 3 is also followed, where the reaction starts with the breaking of the C4–O3 and N9–C5 bonds and the formation of new bonds between C6–O3 and C4–N9. This leads to the formation of the intermediate compound 4-(nitromethyl)-1,3-dioxolane, which in a later stage decomposes through a cyclic transition state of 5 atoms. This involves the migration of hydrogen from carbon 5 and the detachment of the nitro group. The alkene 4-methylene-1,3-dioxolane is also produced by the formation of double bonds at carbons 4 and 5.

Computational optimization of the molecules was accomplished at M06-2X/6–311 + G(d,p). Figure 4 depicts the optimized geometry of the reactants, transition states (TS1-5-H-M1, TS1-5-methyl-M1, and TS1-5-Br-M1) and products (P1-H, P1-methyl, and P1-Br) involved in

the decomposition reactions, following the one-stage mechanism.

Kinetic and thermodynamic parameters

The vibrational frequency data in the temperature range of 503.15–563.15 K obtained with some DFT functionals allowed to calculate the kinetic values are shown in Table 1. It is worth noticing that the lowest activation Gibbs energies (ΔG^\ddagger) for the decomposition reaction are given in their order for the PBE0, ω B97X-D, M06-2X, and MPWB1K functionals.

The results obtained with the PBE0 functional have less overestimation in comparison with the other functionals that were used. Table 2 shows the complete kinetic data calculated with the PBE0 functional and the linearization of the Arrhenius equation.

The two-stage mechanism turned out not to be feasible for the decomposition reaction 5-nitro-1,3-dioxane compared to that occurring in a single-stage mechanism. We see that the first stage is the limiting of the speed with a free energy of activation of 280.6 kJ·mol⁻¹, which is 96.6 kJ·mol⁻¹ higher than the activation free energy in the reaction occurring according to the single-stage mechanism in gas phase.

When the reactions are carried out in solution with DMSO, the energy barrier in each of them is lowered and as a result the decomposition rate increases. The most important solvent effect occurs in the decomposition reaction of 5-methyl-5-nitro-1,3-dioxane, where the activation Gibbs energy is decreased in 17.6 kJ·mol⁻¹. It is also observed that when the substituent is a bromine atom, solvent stabilization is very little.

An important contribution to the decrease of the free energy of activation can be noticed in the activation entropy with the highest value 33.3 J·mol⁻¹·K⁻¹ for bromine as a

Fig. 3 Two-stage mechanism, when the substituent at position 5 is R = H

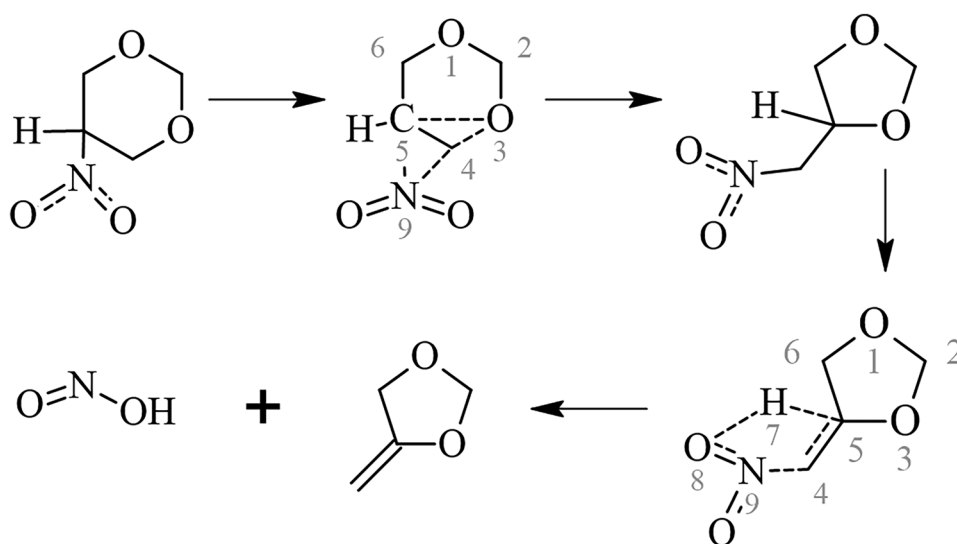
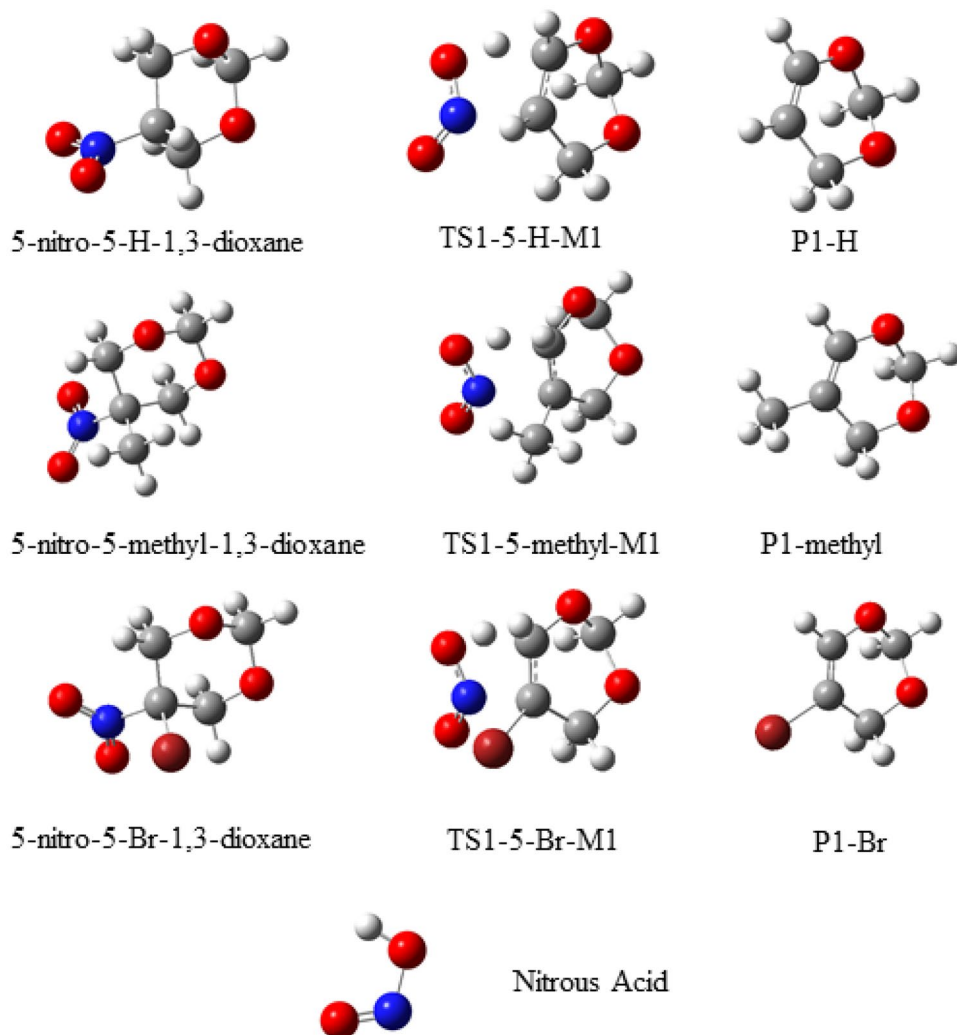


Fig. 4 Molecules optimized for the structure involved in the decomposition reactions by the one-stage mechanism



substituent group in gas phase, which is also evident when looking at the values of the frequency factor (A).

Although the reaction of the molecule with the substituent bromine has higher activation energy (E_a) than the molecule with methyl group substituent, the former has a higher value in the frequency factor (A); therefore, its reaction rate is higher.

Table 1 Gibbs activation energies for the decomposition reaction of 5-R-5-nitro-1,3-dioxane by the one-stage reaction mechanism at 523 K

R group	ΔG^\ddagger (KJ·mol ⁻¹)			
	M06-2X	ω B97X-D	MPWB1K	PBE0
H (gas)	204	192	209	184
H (DMSO)	198	181	200	176
CH ₃ (gas)	194	177	198	183
CH ₃ (DMSO)	175	154	176	165
Br (gas)	199	180	201	173
Br (DMSO)	197	173	194	167

It is also worth noting that the Gibbs energy of activation for the bromine substituent is smaller compared to the corresponding ones for the hydrogen and methyl groups in the gas phase; however, in solution with DMSO, the activation energy becomes smaller for the molecule substituted with a methyl group in position 5.

Figure 5 features the optimized structures involved in the reaction by the proposed two-stage mechanism. Table 3 summarizes the experimental values reported for the modeled decomposition reactions.

The computational findings obtained present some discordance with the experimental values reported by Stepanov et al. [10]. For example, the computational activation energy for the decomposition reaction of the studied compounds are 18, 10, and 16% above the experimental values for the substituent groups H, methyl, and Br, respectively. However, the results reported by the authors indicate that the greatest favorability for decomposition reactions occurs with the bromine atom at position 5, followed by substitution by the methyl group and the

Table 2 PBE0/6–311+G(d,p)-calculated kinetic parameters obtained from computational modeling at 523 K, for thermal decomposition of the studied compounds according to the one-stage mechanism. First inlet gas phase, second inlet solution with DMSO

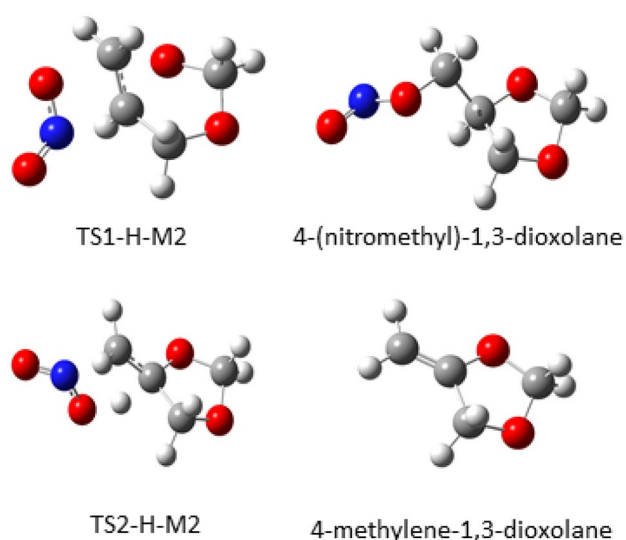
R	ΔG^\ddagger (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)	Log A	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)
H	184.0 (176.1)	204.2 (197.4)	15.1 (15.2)	30.1 (32.2)
H ^a	280.6 (239.4)	–	–	35.6 (38.7)
H ^b	180.7 (170.8)	–	–	11.9 (8.9)
Methyl	182.9 (165.3)	188.3 (174.2)	13.6 (13.9)	2.2 (9.9)
Br	172.9 (167.6)	194.8 (191.7)	15.2 (15.4)	33.3 (37.6)

^aMechanism Fig. 3, stage 1^bMechanism Fig. 3, stage 2

hydrogen atom at position 5. The computational results indicate the same.

The free energy profile for the reaction in gas phase and in DMSO is shown in Fig. 6.

From the graphical representation, it can be observed that the decomposition reaction of 5-bromo-5-nitro-1,3-dioxane generates the most stable products, additional to that kinetically, it is the most favored reaction among the reactions observed. The reactions in DMSO solution occur with a lower activation free energy value; however, the thermodynamics of the reaction are not significantly favored.

**Fig. 5** Gas-phase optimized molecules, according to the two-stage mechanism for R=H. Stage 1 transition state (TS1-H-M2), intermediate 4-(nitromethyl)-1,3-dioxolane. Stage 2 transition state (TS2-H-M2) and 4-methylene-1,3-dioxolane product**Table 3** Experimental kinetic parameters reported [1] in gas phase for the decomposition reactions of the 5-R-5-nitro-1,3-dioxane compounds studied at 523 K

R	Ea (kJ mol ⁻¹)	Log A	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)
H	173.1	12.81	–12.7
Methyl	170.1	13.40	–1.4
Br	167.7	13.42	–1.0

When the reaction is carried out with DMSO solvent, it occurs more quickly, and this is more evident with the methyl group as a substituent.

Population analysis (NBO)

The natural bond orbital (NBO) population partitioning technique was used to obtain the Wiberg bond index values and by means of them to follow in depth the processes of bond breaking and bond formation throughout the chemical reaction.

The findings obtained from the NBO analysis and the other indicators that were calculated with Eqs. (1), (2), (3), and (4) are depicted in Table 4.

The %EV shows us that in the transition state the C–N bond breaking processes are quite advanced processes for the decomposition reactions. We could relate this to an increase in the degrees of freedom of the structure, representing the transition state, and consequently a higher entropy, which fits the kinetic data reported in Table 2.

The methyl substituent at position 5 stabilizes the same carbon, perhaps due to its ability to induce electrons, which is why the C–N bond breaking process is the most advanced, approximately 86% compared to 68% for the H and Br atoms. The substituent at C5 delays the alkene formation and slightly delays oxygen migration as well.

Bromine as a substituent, likely due to its electron-scattering effect, decreases the availability of carbon–carbon double bond formation and increases the advance of O–H and N–O bond formation perhaps due to chain effects on the hydrogen electron cloud.

The average relative variation of the bond indices, $\delta\beta_{av}$, with values of 0.49 and 0.51 for the reactions, indicates symmetric transition states whose structure is intermediate between reactants and products.

The reaction that occurs for the molecule with the methyl substituent presents an imbalance between bond formation and bond breaking events, evidenced by a value of 0.83 for the reaction synchronicity. Perhaps that is why the effect of the solvent is more important for the decomposition of 5-methyl-5-nitro-1,3-dioxane.

Fig. 6 PBE0/6–311+G(d,p)-calculated Gibbs energy profile for the decomposition reaction of 5-nitro-5-R-1,3-dioxane compounds. According to the computationally obtained data for R=H, methyl, and Br

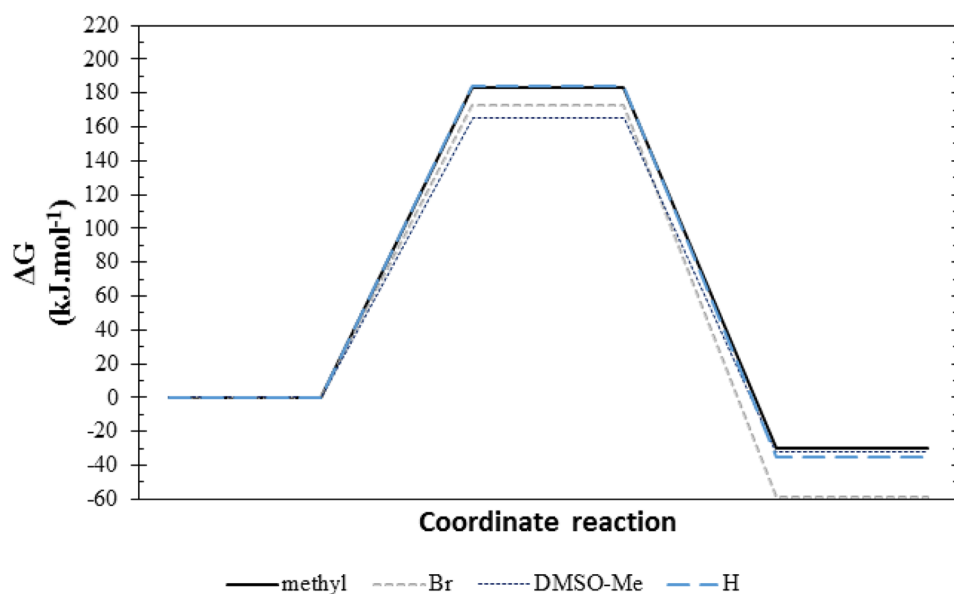


Table 4 Wiberg bond indices for reactants, transition states, and products (B_i^R , B_i^{TS} , and B_i^P) for gas-phase decomposition reactions using the one-stage mechanism

	C ₅ –C ₆	C ₆ –H ₇	H ₇ –O ₈	O ₈ –N ₉	N ₉ –C ₅
B_i^R (1)	0.9793	0.9217	0.0022	1.5178	0.8763
(2)	0.9633	0.9203	0.0025	1.5147	0.8451
(3)	0.9862	0.9083	0.0008	1.5339	0.8408
B_i^{TS} (1)	1.3882	0.4261	0.3176	1.372	0.278
(2)	1.3524	0.4393	0.3006	1.3743	0.1187
(3)	1.3527	0.4249	0.3183	1.371	0.2694
B_i^P (1)	1.8559	0.0000	0.752	1.0947	0.0000
(2)	1.8092	0.0000	0.752	1.0947	0.0000
(3)	1.795	0.0000	0.752	1.0947	0.0000
%EV (1)	46.65	53.77	42.06	34.46	68.28
(2)	46.00	52.27	39.77	33.43	85.95
(3)	45.31	53.22	42.27	37.09	67.96
		$\delta\beta_{av}$ =	(1) 0.49	S_y =	(1) 0.88
			(2) 0.51		(2) 0.83
			(3) 0.49		(3) 0.88

(1) R=H, (2) R=Me, (3) R=Br

%EV percentage of evolution, $\delta\beta_{av}$ average relative variation, S_y absolute synchronicity of the reaction

Conclusions

Computational calculations with the M06-2X, MPWB1K, PBE0, and ω B97X-D functionals were performed to model the decomposition reaction of the 5-nitro-5-R-1,3-dioxane compounds. The comparison of the results obtained with the experimental ones indicates that the functional PBE0 better describes the reaction system.

Two possible reaction mechanisms for the thermal decomposition of 5-nitro-1,3-dioxane were considered. The findings of the computational calculations indicate that the two-stage mechanism for this reaction is not feasible with respect to the single-stage mechanism. When this compound is substituted at the carbon 5 position by a methyl group or a bromine atom, the rate of the reaction becomes higher, mainly with the bromine group, and if the reaction is also carried out in solution with a solvent such as DMSO, the activation energy decreases with respect to the reaction in the gas phase.

The values of kinetic and thermodynamic parameters obtained in this study and through the density functional theory, depart from the experimental values previously reported by Stepanov et al. [10]. However, there is an agreement regarding the effect of substituent groups on the reaction.

The analysis of the Wiberg bond indices for the reaction studied allowed us to define carbon–nitrogen and nitrogen–oxygen bond breaking as the most and least advanced processes in each of the reactions, respectively.

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1007/s11224-022-01891-6>.

Acknowledgements The authors are grateful for the support received from the Universidad Nacional de Colombia – Medellín Headquarters during the research and publication stages of this work. S. Q. also thanks Dirección General de Investigaciones of Universidad Santiago de Cali (DGI), Santiago de Cali. P. R. also thanks Instituto Tecnológico Metropolitano (ITM).

Author contribution The contribution of each author listed is based on Silvia Quijano and Pablo Ruiz, who made a substantial contribution to the conception and design, data acquisition and analysis, and interpretation of the data; Pablo Ruiz and Jairo Quijano drafted the article and

critically reviewed the intellectual content. All the authors read and approved the final manuscript.

Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

References

- Carrera G, Vegué L, Boleda MR, Ventura F (2017) Simultaneous determination of the potential carcinogen 1,4-dioxane and malodorous alkyl-1,3-dioxanes and alkyl-1,3-dioxolanes in environmental waters by solid-phase extraction and gas chromatography tandem mass spectrometry. *J Chromatogr A* 1487:1–13
- Kuramshina AE, Kuznetsov VV (2010) Quantum-chemical study of 1,3-dioxane complexes with two water molecules. *Russ J Org Chem* 46:665–669
- Zeng L, Xu G, Gao P, Zhang M, Li H, Zhang J (2015) Design, synthesis and evaluation of a novel class of glucosamine mimetic peptides containing 1,3-dioxane. *Eur J Med Chem* 93:109–120
- Wong JC, Sternson SM, Louca JB, Hong R, Schreiber SL (2004) Modular synthesis and preliminary biological evaluation of stereochemically diverse 1,3-dioxanes. *Chem Biol* 11:1279–1291
- Lapass LC, Hirsch CA, Winely CL (1976) Substituted 5-nitro-1,3-dioxanes: correlation of chemical structure and antimicrobial activity. *J Pharm Sci* 65:1301–1305
- Adelaide T, Adebayo W, Russell B, Salt WG (1987) Radical-nucleophilic substitution (SRN1) reactions. Part 5. Anions of nitroimidazoles in SRN1 and oxidative addition reactions. *J Chem Soc Perkin Trans I*:2819–2827
- Fernandez-Alvarez M, Lamas JP, Sanchez-Prado L, Llompert M, Garcia-Jares C, Lores M (2010) Development of a solid-phase microextraction gas chromatography with microelectron-capture detection method for the determination of 5-bromo-5-nitro-1,3-dioxane in rinse-off cosmetics. *J Chromatogr A* 1217:6634–6639
- Stepanov RS, Kruglyakova LA, Astakhov AM, Golubtsova OA (2004) Kinetics and mechanism of thermal decomposition of 2-substituted 5,5-dinitro-1,3-dioxanes. *Russ J Gen Chem* 74:1579–1582
- Lytko-Krasuska A, Piotrowska H, Urbanski T (1979) Reductive elimination of a tertiary nitro group in 5-nitro-1,3-dioxanes. *Tetrahedron Lett* 20:1243–1246
- Stepanov RS, Kruglyakova LA, Golubtsova OA (2011) Kinetics of thermolysis of 5-nitro-5-R-1,3-dioxanes. *Russ J Gen Chem* 81:151–152
- Kupova OY, Vakulin IV, Talipov RF (2013) Ab initio study of 1,3-dioxanes formation from formaldehyde dimer and alkenes. *Comput Theor Chem* 1013:57–61
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2010) Gaussian 09, Revision B.01, Gaussian Inc., Wallingford CT
- Zhao Y, Truhlar DG (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. *Theor Chem Acc* 120:215–241
- Ditchfield R, Hehre WJ, Pople JA (1971) Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *J Chem Phys* 54:724–728
- Zhao Y, Truhlar DG (2004) Hybrid meta density functional theory methods for thermochemistry, thermochemical kinetics, and non-covalent interactions: the MPWB1B95 and MPWB1K models and comparative assessments for hydrogen bonding and van der Waals interactions. *J Phys Chem A* 108:6908–6918
- Adamo C, Barone V (1999) Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J Chem Phys* 110:6158–6170
- Chai JD, Head-Gordon M (2008) Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys Chem Chem Phys* 10:6615–6620
- Merrick JP, Moran D, Radom L (2007) An evaluation of harmonic vibrational frequency scale factors. *J Phys Chem A* 111:11683–11700
- McQuarrie DA, Simon JD (1999) *Molecular thermodynamics*. University Science Books, Sausalito, CA
- Tomasi J, Mennucci B, Cammi R (2005) Quantum mechanical continuum solvation models. *Chem Rev* 105:2999–3094
- Fukui K (1970) A formulation of the reaction coordinate. *J Phys Chem* 74:4161–4163
- Glasstone S, Laidler K, Eyring H (1941) In: *The theory of rate processes*, 1st edn. McGraw Hill, New York
- Benson SW (1969) *The Foundations of chemical kinetics*. McGraw-Hill, New York
- Reed AE, Weinhold FJ (1983) Natural bond orbital analysis of near-Hartree–Fock water dimer. *Chem Phys* 78:4066–4073
- Reed AE, Curtiss LA, Weinhold F (1988) Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem Rev* 88:899–926
- Glendening ED, Reed AE, Carpenter JE, Weinhold F (1988) NBO Version 3.1. Madison WI
- Wiberg KB (1968) Application of the pople-santry-segal CNDO method to the cyclopropylcarbanyl and cyclobutyl cation and to bicyclobutane. *Tetrahedron* 24:1083–1096
- Moyano A, Pericas MA, Valentí E (1989) A theoretical study on the mechanism of the thermal and the acid-catalyzed decarboxylation of 2-oxetanones (β -lactones). *J Org Chem* 54:573–582

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.