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A density functional theory study of the gas-phase elimination reactions of 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones and their 3(2*H*)-thione analogues

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Abstract. Theoretical studies on the thermolysis in the gas phase of 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones and 4-arylideneimino-1,2,4-triazol-3(2*H*)-thiones were carried out using density functional theory methods, at the B3LYP/6-31G(d) and B3LYP/6-311+G(2d,p) levels of theory. The proposed reaction mechanism occurs in one step, leading to the formation of 3-hydroxy-(2*H*)-1,2,4-triazole or 3-mercapto-(2*H*)-1,2,4-triazole and a 4-substituted benzonitrile, via a six-membered cyclic transition state. The progress of the reactions was followed by means of the Wiberg bond indices. The results indicate that the transition states have character intermediate between reactants and products, and the calculated synchronicities show that the reactions are slightly asynchronous, in the case of triazolones, and show a higher asynchronicity in the case of triazolthiones. The bond-breaking processes are slightly more advanced than the bond-forming ones, indicating a small bond deficiency in the transition states. Kinetic and activation parameters for the reactions studied have been calculated and compared with available experimental data.

Keywords: 4-Arylideneimino-1,2,4-triazol-3(2*H*)-ones – 4-Arylideneimino-1,2,4-triazol-3(2*H*)-thiones – Thermal decomposition – Density functional theory – Reaction mechanism

Introduction

In the last few years we have been involved [1, 2, 3, 4, 5] in the theoretical study of the mechanisms of several thermolysis reactions in the gas phase, and have compared the results with available experimental data. Following this work we have carried out a study on the gas-phase pyrolyses of some 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones and the corresponding 3(2*H*)-thiones (Fig. 1). An experimental study on these reactions was carried out very recently by Al-Awadi et al. [6].

Al-Awadi et al. [7] have pointed out that this reaction is an alternative approach for the conversion of aldehydes into nitriles via the pyrolysis of Schiff bases obtained by condensing aldehydes with *N*-amino heteroaromatics [8]. The most widely used route is conversion of aldehydes into oximes followed by dehydration [9, 10, 11], but this approach is not suitable for synthesis of nitriles with functional substituents that are unstable under various reaction conditions [7].

The reactions studied were ascertained to be homogeneous, unimolecular and free of reaction surface effects. According to the products of the reactions, the authors suggested [6] that the pathway of the reactions involves a concerted cyclic six-membered transition state, as shown in Fig. 1.

The aim of this work was to carry out a computational study in order to explore the nature of the reaction mechanism for the gas-phase unimolecular decomposition of several triazolones and triazolthiones: 4-benzylideneimino-1,2,4-triazol-3(2*H*)-one, I; 4-*p*-chlorobenzylideneimino-1,2,4-triazol-3(2*H*)-one, II; 4-*p*-methylbenzylideneimino-1,2,4-triazol-3(2*H*)-one, III; 4-*p*-methoxybenzylideneimino-1,2,4-triazol-3(2*H*)-one,

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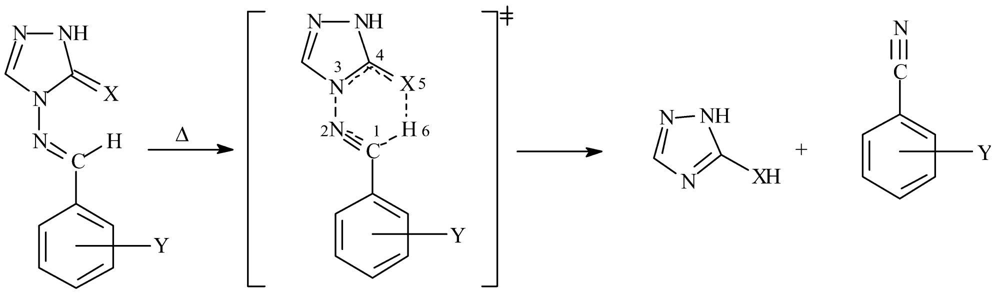

I X = O Y = H
II X = O Y = 4-Cl
III X = O Y = 4-Me
IV X = O Y = 4-OMe
V X = S Y = H
VI X = S Y = 4-Cl
VII X = S Y = 4-Me
VIII X = S Y = 4-OMe

Fig. 1. Mechanism for the decomposition of 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones, I–IV, and 4-arylideneimino-1,2,4-triazol-3(2*H*)-thiones, V–VIII

IV; 4-benzylideneimino-1,2,4-triazol-3(2*H*)-thione, V; 4-*p*-chlorobenzylideneimino-1,2,4-triazol-3(2*H*)-thione, VI; 4-*p*-methylbenzylideneimino-1,2,4-triazol-3(2*H*)-thione, VII; and 4-*p*-methoxybenzylideneimino-1,2,4-triazol-3(2*H*)-thione, VIII. To our knowledge, this is the first theoretical study on the thermolysis reaction of these types of compounds. The only structural feature which distinguishes both types of compounds is the greater protophilicity and lability together with the relative thermodynamic stability and π-bond energy difference of the thiocarbonyl and carbonyl bonds [6].

Computational details

Density functional calculations were performed with the Gaussian98 series of programs [12]. Among the various functionals proposed, we used the combination of Becke's three-parameter hybrid exchange functional [13] with the Lee, Yang and Parr correlation functional [14], denoted B3LYP [15].

The geometric parameters for all the reactants, the transition states (TSs), and the products of the reactions studied were fully optimized at the B3LYP/6-31G(d) level [16]. Each stationary structure was characterized as a minimum or a saddle point of first order by analytical frequency calculations. A scaling factor [17] of 0.9806 for the zero-point vibrational energies was used. Thermal corrections to enthalpy and entropy values were evaluated at the experimental temperature of 500.15 K. To calculate enthalpy and entropy values at a temperature *T*, the difference between the values at that temperature and at 0 K was evaluated according to standard thermodynamics [18].

Intrinsic reaction coordinate calculations [19] were performed in all cases to verify that the localized TS structures connect with the corresponding minimum stationary points associated with reactants and products.

Single-point energy calculations at the B3LYP/6-311 + G(2d,p) level [20] were performed on the B3LYP/6-31G(d)-optimized structures for all the reactants, TSs, and products, to calculate reliable energy profiles and kinetic parameters.

The bonding characteristics of the different reactants, TSs, and products were investigated using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold [21, 22]. The NBO formalism provides the Wiberg bond indices [23] used to follow the progress of the reactions. The NBO analysis was performed using the NBO program [24], implemented in the Gaussian98 package [12], and was carried out on the B3LYP charge densities in order to explicitly include electron correlation effects.

We selected the classical TS theory (TST) [25, 26] to calculate the kinetic parameters. The rate constant, $k(T)$, for each elementary step of the kinetic scheme (Fig. 2) was computed using this theory assuming that the transmission coefficient is equal to unity, as expressed by the following relation:

$$k(T) = \frac{k_\mathrm{B}T}{h} \exp\left(\frac{-\Delta G^{\neq}(T)}{RT}\right), \tag{1}$$

where k_B, h and R are the Boltzmann constant, the Planck constant, and the universal gas constant, respectively. $\Delta G^{\neq}(T)$ is the standard-state free energy of activation, at the absolute temperature T.

The activation energies, E_a and the Arrhenius A factors were calculated using Eqs. (2) and (3), respectively, derived from the TST theory:

$$E_\mathrm{a} = \Delta H(T) + RT, \tag{2}$$

$$A = \frac{ek_\mathrm{B}T}{h} \exp\left(\frac{\Delta S^{\neq}(T)}{R}\right). \tag{3}$$

Results and discussion

Electronic energies, evaluated at the B3LYP/6-31G(d) and B3LYP/6-311 + G(2d,p)//6-31G(d) levels of theory, and zero-point vibrational energies, thermal correction

Fig. 2. Free-energy profiles at 500.15 K, evaluated at the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) level, for the decomposition processes: **a** I and **b** V

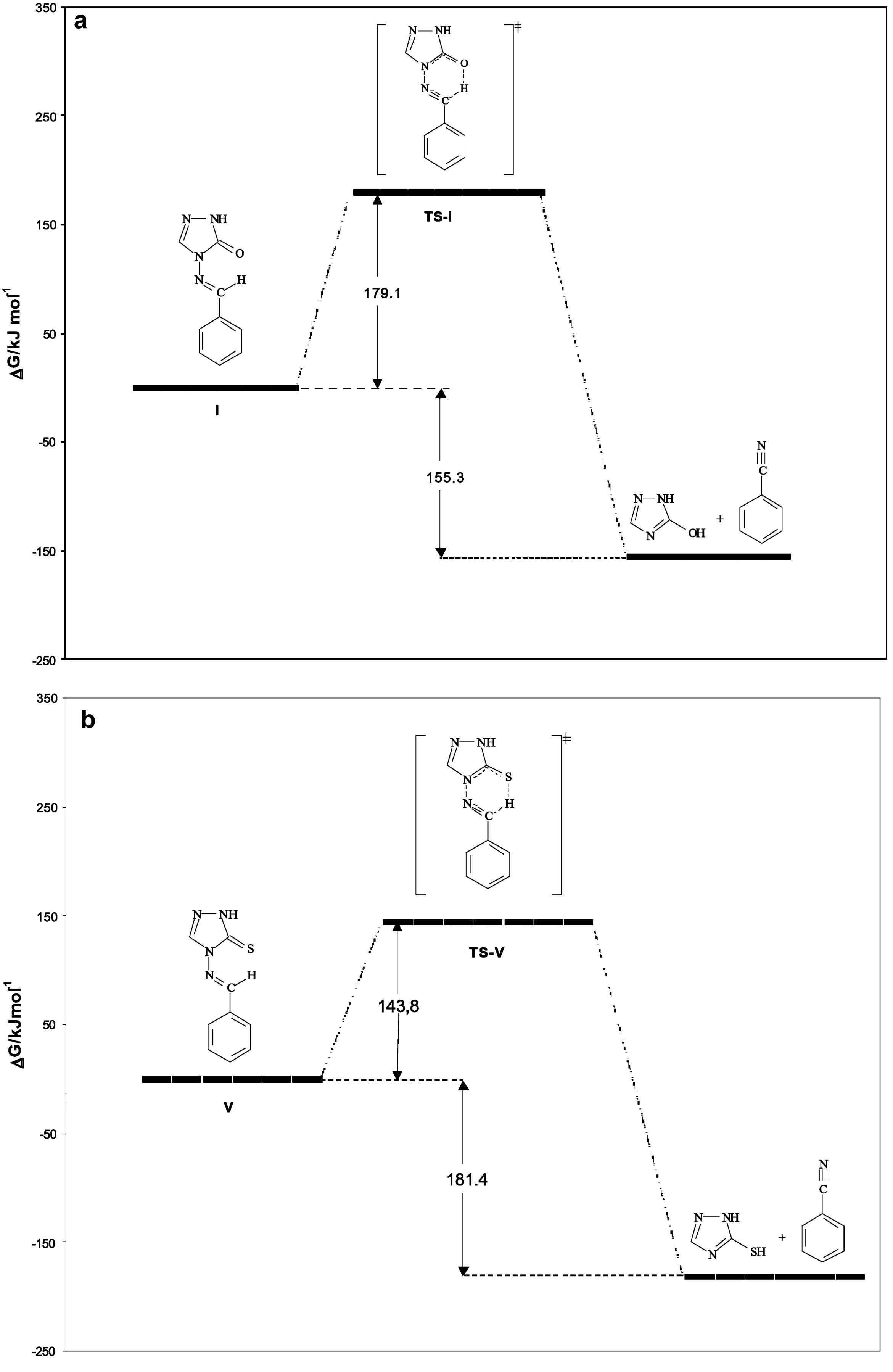
a
ΔG/kJ mol-1
350
250
150
50
-50
-150
-250
‡
TS-I
I
179.1
155.3
+
b
ΔG/kJmol-1
350
250
150
50
-50
-150
-250
‡
TS-V
V
143,8
181.4
+

Table 1. Electronic energies, evaluated at the B3LYP/6-31G(d) and B3LYP/6-311 + G(2d,p) levels, zero-point vibrational energies (*ZPE*) and thermal corrections to enthalpies (*TCH*) in hartrees, and entropies, *S*, in joules per mole per Kelvin, for all the reactants, transition states and products involved in the reactions studied

Species	B3LYP/ 6-31G(d)	B3LYP/6-311 + G(2d,p)/ B3LYP/6-31G(d)	ZPE	TCH	*S*
I	−641.963855	−642.154652	0.166981	0.197528	632.40
TS-I	−641.885373	−642.079119	0.159684	0.190258	634.93
II	−1,101.559599	−1,101.779505	0.157276	0.190230	669.97
TS-II	−1,101.480125	−1,101.703269	0.149906	0.182916	673.70
III	−681.282493	−681.484029	0.194437	0.229250	697.06
TS-III	−681.204302	−681.408820	0.187218	0.221998	693.87
IV	−756.488245	−756.716108	0.199741	0.236409	709.78
TS-IV	−756.410327	−756.641241	0.192601	0.229201	709.00
V	−964.922518	−965.112715	0.164882	0.195999	646.52
TS-V	−964.859786	−965.052748	0.159085	0.189924	642.44
VI	−1,424.518070	−1,424.737486	0.155179	0.188695	683.04
TS-VI	−1,424.454527	−1,424.676861	0.149312	0.182558	680.03
VII	−1,004.241289	−1,004.442201	0.192363	0.227713	706.45
TS-VII	−1,004.178731	−1,004.382430	0.186630	0.221666	699.27
VIII	−1,079.447320	−1,079.674507	0.197686	0.234915	724.99
TS-VIII	−1,079.384761	−1,079.614785	0.191905	0.228835	718.23
3-Hydroxy-(2*H*)-1,2,4-traizole	−317.471788	−317.581045	0.064457	0.077527	407.88
3-Mercapto-(2*H*)-1,2,4-traizole	−640.435338	−640.543805	0.058846	0.073254	433.79
Benzonitrile	−324.492216	−324.585789	0.099444	0.116929	456.88
4-Chloro-benzonitrile	−784.086701	−784.209561	0.089757	0.109608	494.94
4-Methylbenzonitrile	−363.811139	−363.915368	0.126953	0.148649	523.74
4-Methoxybenzonitrile	−439.016826	−439.147490	0.132263	0.155813	539.69

to enthalpies and entropies, obtained at the B3LYP/6-31G(d) level, for all the reactants, TSs and products involved in the reactions studied are collected in Table 1.

The suggested reaction pathway (Fig. 2) describes an one-step mechanism. The pyrolysis of the compounds studied leads to 3-hydroxy-(2*H*)-1,2,4-triazole or 3-mercapto-(2*H*)-1,2,4-triazole and the corresponding 4-substituted benzonitrile, via a six-membered cyclic TS, where the N–N bond is breaking and the hydrogen atom attached to C_1 is migrating to the oxygen (or sulfur) atom of the carbonyl (or thiocarbonyl) group of the triazole ring.

Free-energy reaction profiles were obtained at the B3LYP/6-311 + G(2d,p)//6-31G(d) level of theory. The profiles for the decomposition processes of the unsubstituted compounds studied, I and V, are presented in Fig. 2. The overall processes are highly exergonic, with reaction free energies of −155.3, −153.6, −157.5, and −159.5 kJ mol^{-1}, for reactions I, II, III, and IV, respectively, and of −181.4, −179.6, −185.1, and −183.4 kJ mol^{-1}, for reactions V, VI, VII, and VIII, respectively.

There is only one imaginary vibrational frequency in the TSs, optimized at the B3LYP/6-31G(d) level of theory. All the optimized structures for the reactants and products are planar; however, the geometries found for the TSs are not planar—some of them are shown in Fig. 3.

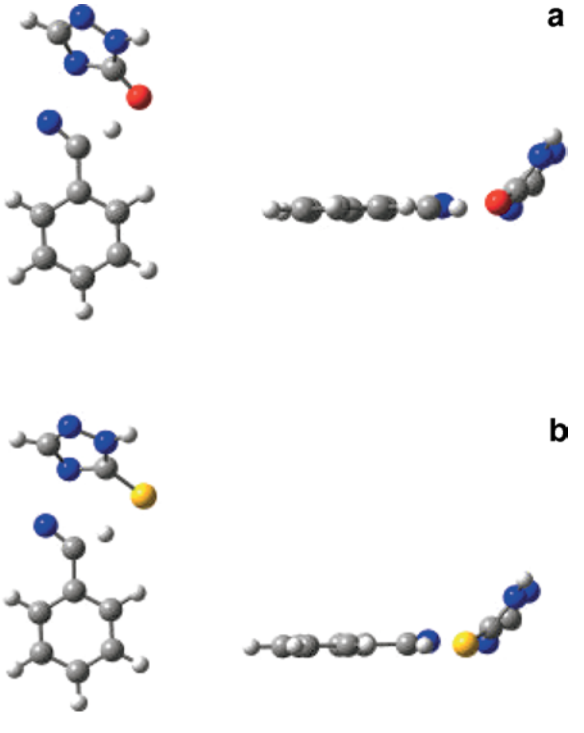

Fig. 3. Transition states, optimized at the B3LYP/6-31G(d) level, from two different views: **a** TS-1 and **b** TS-V

The results listed in Table 2 show the main distances for each optimized structure. During the thermolysis process, when the reactant is being transformed into its TS, the C_1–N_2, N_3–C_4 and X_5–H_6 distances decrease, whereas the N_2–N_3, C_4–X_5 and H_6–C_1 distances increase. The fundamental characteristics in this process are the N_2–N_3 (1.37–1.38 Å) and X_5–H_6 (2.18–2.19 Å for O–H, in I–IV, and 2.48 Å for S–H, in V–VIII) distances for each reactant. In the corresponding TSs, the N_2–N_3 distance increases significantly (2.11–2.13 Å), by the breaking of this bond, while the X_5–H_6 distance decreases significantly (1.36–1.38 Å, for O–H, in I–IV, and 1.84–1.86 Å for S–H, in V–VIII), by the formation of this bond.

The progress of the reactions was followed by means of the Wiberg bond indices [23], B_i, defined as

Table 2. Main distances, in angstroms, in the reactants, transition states and products of the reactions, calculated at the B3LYP/6-31G(d) level

	C_1–N_2	N_2–N_3	N_3–C_4	C_4–X_5	X_5–H_6	H_6–C_1
I	1.290	1.374	1.419	1.222	2.186	1.089
TS-I	1.224	2.126	1.362	1.275	1.371	1.245
II	1.290	1.372	1.420	1.222	2.182	1.089
TS-II	1.225	2.118	1.361	1.276	1.358	1.252
III	1.290	1.375	1.419	1.222	2.188	1.089
TS-III	1.225	2.129	1.362	1.274	1.376	1.243
IV	1.291	1.376	1.418	1.223	2.185	1.089
TS-IV	1.226	2.131	1.361	1.274	1.378	1.241
V	1.289	1.378	1.401	1.674	2.479	1.088
TS-V	1.227	2.107	1.351	1.712	1.852	1.202
VI	1.289	1.376	1.402	1.673	2.475	1.088
TS-VI	1.226	2.108	1.351	1.712	1.844	1.205
VII	1.290	1.379	1.401	1.674	2.480	1.088
TS-VII	1.227	2.108	1.351	1.712	1.854	1.202
VIII	1.291	1.380	1.400	1.675	2.477	1.088
TS-VIII	1.228	2.110	1.350	1.712	1.855	1.202
3-Hydroxy-(2*H*)-1,2,4-traizole	–	–	1.317	1.341	0.972	–
3-Mercapto-(2*H*)-1,2,4-traizole	–	–	1.322	1.766	1.347	–
Benzonitrile	1.163	–	–	–	–	–
4-Chlorobenzonitrile	1.163	–	–	–	–	–
4-Methylbenzonitrile	1.164	–	–	–	–	–
4-Methoxybenzonitrile	1.164	–	–	–	–	–

the sum of the squares of the off-diagonal density matrix elements between atoms. The bond index between two atoms is a measure of the bond order and, hence, of the bond strength between these two atoms. Thus, if the evolution of the bond indices corresponding to the bonds being made or broken in a chemical reaction is analyzed along the reaction path, a very precise image of the timing and extent of the bond-breaking and the bond-making processes at every point can be achieved [27].

The Wiberg bond indices corresponding to the bonds being made or broken in the reactions studied, for the reactants, TSs, and products, are collected in Table 3.

In order to perform the bond index analysis, it is convenient to define [27] a relative variation of the bond index at the TS, δB_i, for every bond, i, involved in a chemical reaction as

$$\delta B_i = \frac{\left(B_i^{\mathrm{TS}} - B_i^{\mathrm{R}}\right)}{\left(B_i^{\mathrm{P}} - B_i^{\mathrm{R}}\right)}, \tag{4}$$

where the superscripts R, TS and P refer to reactants, TSs and products, respectively.

The percentage of evolution, %EV, of the bond order through the chemical step was calculated [28] by means of

$$\%EV = 100\delta B_i \tag{5}$$

and the values are collected in Table 3.

As can be seen in that table, the breaking of the N_2–N_3 bond is the most advanced process (67% in all the reactions). Also advanced are the N_3–C_4 double-bond formation and the C_4–X_5 double-bond breaking. The less advanced ones are the C_1–N_2 triple-bond formation (38–40%) and overall the H_6 migration from C_1 to X_5 (The C_1–H_6 bond is broken in 40–41% of cases in the oxotriazoles I–IV, and only in 31–32% of cases in the thiotriazoles V–VIII, while the X_5–H_6 bond is formed in 35–37% of cases in the oxotriazoles I-IV, and only in 30–31%of cases in the thiotriazoles V–VIII). So, the elongation of the N_2–N_3 bond seems to be the driving force for the reactions studied, instead of the migration of the H_6 atom from C_1 to X_5.

The average value, δB_{av}, calculated [27] as:

$$\delta B_{\mathrm{av}} = \frac{1}{n}\sum \delta B_i, \tag{6}$$

where n is the number of bonds involved in the reaction, affords a measure of the degree of advancement of the TS along the reaction path.

Calculated δB_{av} values for the studied reactions are shown in Table 3. As can be seen in this table, the δB_{av} values, ranging from 0.47 to 0.49, show that the TSs have character intermediate between the reactants and the products, but slightly nearer to the reactants.

One can also obtain information on the absolute asynchronicity, A, of a chemical reaction, using the expression proposed by Moyano et al. [27]:

$$A = \frac{1}{(2N-2)}\sum \frac{|\delta B_i - \delta B_{\mathrm{av}}|}{\delta B_{\mathrm{av}}}. \tag{7}$$

The opposite of the asynchronicity, the synchronicity, Sy, defined as

$$\mathrm{Sy} = 1 - A, \tag{8}$$

varies between zero, when one of the n bonds has completely broken at the TS while the other n–1 bonds remain completely unchanged, and unity, when all the n bonds have broken or formed to exactly the same extent in the TS.

Table 3. Wiberg bond indices,B_i, of reactants, transition states and products of the reactions studied, percentage of evolution (*%EV*) through the chemical process of the bond indices at the transition states, degree of advancement of the transition states, δB_{av}, and absolute synchronicities (*Sy*). Values calculated at the B3LYP/6-31G(d) level

		C_1–N_2	N_2–N_3	N_3–C_4	C_4–X_5	X_5–H_6	H_6–C_1
Reaction I	B_i^R	1.734	1.082	0.998	1.618	0.012	0.893
	$B_i^{\ddagger S}$	2.191	0.357	1.257	1.319	0.264	0.536
	B_i^P	2.864	0.000	1.467	1.048	0.712	0.000
	%EV	40.4	67.0	55.2	52.5	36.0	40.0
				$\delta B_{av} = 0.485$			
				Sy = 0.880			
Reaction II	B_i^R	1.732	1.085	0.996	1.620	0.013	0.892
	$B_i^{\ddagger S}$	2.191	0.362	1.258	1.313	0.272	0.527
	B_i^P	2.865	0.000	1.467	1.048	0.712	0.000
	%EV	40.5	66.6	55.6	53.7	37.1	40.9
				$\delta B_{av} = 0.491$			
				Sy = 0.883			
Reaction III	B_i^R	1.730	1.080	0.999	1.617	0.012	0.893
	$B_i^{\ddagger S}$	2.186	0.355	1.257	1.320	0.262	0.538
	B_i^P	2.862	0.000	1.467	1.048	0.712	0.000
	%EV	40.3	67.1	55.1	52.2	35.7	39.8
				$\delta B_{av} = 0.484$			
				Sy = 0.879			
Reaction IV	B_i^R	1.722	1.077	1.001	1.614	0.013	0.893
	$B_i^{\ddagger S}$	2.174	0.354	1.258	1.320	0.260	0.540
	B_i^P	2.856	0.000	1.467	1.048	0.712	0.000
	%EV	39.9	67.1	55.2	51.9	35.3	39.5
				$\delta B_{av} = 0.482$			
				Sy = 0.877			
Reaction V	B_i^R	1.720	1.079	1.076	1.483	0.024	0.883
	$B_i^{\ddagger S}$	2.161	0.354	1.319	1.264	0.305	0.606
	B_i^P	2.864	0.000	1.476	1.084	0.951	0.000
	%EV	38.5	67.2	60.8	54.9	30.3	31.4
				$\delta B_{av} = 0.472$			
				Sy = 0.825			
Reaction VI	B_i^R	1.719	1.082	1.074	1.486	0.025	0.882
	$B_i^{\ddagger S}$	2.163	0.354	1.319	1.263	0.311	0.602
	B_i^P	2.865	0.000	1.476	1.084	0.951	0.000
	%EV	38.7	67.3	60.9	55.5	30.9	31.7
				$\delta B_{av} = 0.475$			
				Sy = 0.827			
Reaction VII	B_i^R	1.715	1.078	1.078	1.481	0.024	0.883
	$B_i^{\ddagger S}$	2.156	0.354	1.320	1.264	0.304	0.607
	B_i^P	2.862	0.000	1.476	1.084	0.951	0.000
	%EV	38.4	67.2	60.8	54.7	30.2	31.3
				$\delta B_{av} = 0.471$			
				Sy = 0.824			
Reaction VIII	B_i^R	1.705	1.076	1.081	1.475	0.025	0.883
	$B_i^{\ddagger S}$	2.144	0.352	1.321	1.263	0.303	0.607
	B_i^P	2.856	0.000	1.476	1.084	0.951	0.000
	%EV	38.1	67.3	60.8	54.2	30.0	31.3
				$\delta B_{av} = 0.470$			
				Sy = 0.824			

The Sy values obtained in this way are, in principle, independent of the degree of advancement of the TS. The Sy values calculated for the reactions studied are shown in Table 3. As can be seen in that table, the synchronicities are different in the two series of compounds studied, 0.88 in the case of oxotriazoles I–IV, and only 0.82–0.83 in the case of thiotriazoles V–VIII. These values indicate that the mechanisms correspond to slightly asynchronous processes in the case of compounds I–IV, and more asynchronous processes in the case of compounds V–VIII.

A last aspect to be taken into account is the relative asynchronicity of the bond-breaking and the bond-forming processes that would be a measure of "bond deficiency" along the reaction path. In the reactions studied, the bond-breaking processes are slightly more

Table 4. Theoretical [evaluated at the B3LYP/6-311 + G(2d,p)//6-31G(d) level] and experimental (values taken from Ref. [6]) kinetic and activation parameters for the pyrolysis of the compounds studied, at 500.15 K

Reaction	10^5 k (s^{-1})		E_a (kJ mol^{-1})		log$A$		$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Calc	Calc
I	0.209	0.235	184.6	174.6 ± 2.5	13.6	12.6 ± 0.2	180.4	179.1	2.5
II	0.190	0.219	185.5	172.4 ± 2.1	13.6	12.4 ± 0.2	181.3	179.5	3.7
III	0.153	0.280	183.0	171.0 ± 0.9	13.3	12.3 ± 0.1	178.8	180.4	−3.2
IV	0.247	0.815	182.2	142.1 ± 2.4	13.4	9.8 ± 0.2	178.0	178.4	−0.8
V	1,010	483	146.0	124.3 ± 0.8	13.2	10.7 ± 0.1	141.8	143.8	−4.1
VI	778	520	147.6	127.5 ± 0.4	13.3	11.0 ± 0.1	143.4	144.9	−3.0
VII	778	705	145.5	154.8 ± 0.1	13.1	14.02 ± 0.01	141.3	1449	−7.2
VIII	856	475	145.3	156.7 ± 0.2	13.1	14.05 ± 0.02	141.1	144.5	−6.8

advanced (an average of 52%) than the bond-forming ones (an average of 44%), indicating a small bond deficiency in the TSs.

The calculated kinetic and activation parameters for the reactions studied, evaluated at the B3LYP/6-311 + G(2d,p)//6-31G(d) level of theory, are shown in Table 4 and are compared with the available experimental results. They were calculated at the same temperature and pressure used in the experiments, 500.15 K and 0.0004 atm.

As can be seen in Table 4, there are some discrepancies between experimental and calculated E_a and log$A$ values. While the calculated log$A$ values are very similar for all the reactions, ranging from 13.1 to 13.6, the experimental log$A$ values differ considerably from one reaction to another, ranging from 9.8 to 14.05, and there is no any pattern in both series of reactions, so while the minimum value corresponds to reaction of compound IV, the maximum value corresponds to reaction of compound VIII, both of them with the same substituent, *p*-methoxy.

A similar situation occurs in the case of E_a values. The calculated values follow the same behavior in both series of reactions, the order with respect to the substituents being p-OMe < p-Me < H < p-Cl. This is the same order as that of the σ_p parameter for these substituents.[1] The experimental E_a values do not follow a clear behavior, and so the values for reactions I, II and III are similar, but for reaction IV the value is very different. In triazolthiones, the E_a values for reactions V and VI are similar but are very different from those obtained for reactions VII and VIII.

As a consequence of these discrepancies, in the case of the rate constants the agreement, in particular for the triazolones, point by point is not bad, but in relative terms is not good at all. The reactivity of the substituted triazolthiones is 3.5−5×10^3 times greater than that of triazolones, taking into account the calculated values.

Conclusions

A theoretical study on the thermal decomposition in the gas phase of several 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones and 4-arylideneimino-1,2,4-triazol-3(2*H*)-thiones was carried out in order to explore the nature of the reaction mechanisms.

The decomposition process in the gas phase of these compounds was studied supposing a mechanism in one step, the products being 3-hydroxy-(2*H*)-1,2,4-triazole or 3-mercapto-(2*H*)-1,2,4-triazole and a 4-substituted benzonitrile, via a six-membered cyclic TS, as shown by the free-energy profiles.

The progress of the reactions was followed by means of the Wiberg bond indices. The elongation of the N_2−N_3 bond can be seen as the driving force for the reactions studied. The TSs have character intermediate between reactants and products, but slightly nearer to the reactants. The calculated synchronicities show that the reactions are slightly asynchronous in the case of the triazolones studied, and show a higher asynchronicity in the case of triazolthiones. The bond-breaking processes are slightly more advanced than the bond-forming ones, indicating a small bond deficiency in the TSs.

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[1] The σ_p values for p-OMe, p-Me, H and p-Cl are −0.27, −0.17, 0.00 and 0.23, respectively, taken from Ref. [29]

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