Cent. Eur. J. Chem. • 11(9) • 2013 • 1471-1480
DOI: 10.2478/s11532-013-0276-6

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Central European Journal of **Chemistry**

An experimental and theoretical study of the polar [2+3] cycloaddition reactions between 1-chloro-1-nitroethene and (Z)-C-aryl-N-phenylnitrones[†]

Research Article

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Received 6 March 2013; Accepted 6 May 2013

Abstract: Kinetic studies and B3LYP/6-31g(d) calculations indicate the polar nature of [2+3] cycloadditions between 1-chloro-1-nitroethene to (Z)-C-aryl-N-phenylnitrones. This is clearly confirmed by the activation parameters and the substituent and solvent effects.

Keywords: *[2+3] cycloaddition • Nitrone • Kinetic study • DFT calculations • Global nucleophilicity*

1. Introduction

Knowledge of the mechanism of [2+3] cycloadditions has evolved a lot in the last twenty-five years, from the view that a concerted mechanism was the only one possible [2] to acceptance of the possibility of zwitterionic or diradical intermediates on the reaction pathways [3,4]. Currently, it is known that the zwitterionic mechanism occurs for certain cycloadditions involving azides [5], thiocarbonyl ylides [6-8], azomethine ylides [9], and probably diazo compounds [10] and nitrile N-oxides [11,12]. However, there are no documented examples in the literature of a zwitterionic [2+3] cycloaddition mechanism for nitrones. Although B3LYP/6-31g(d) simulations suggest a zwitterionic mechanism of the cycloaddition of *gem*-dinitroethene with (Z)-C,N-diphenylnitrone [13], the low stability of this nitroalkene prevents the experimental verification of theoretical conclusions. Therefore, continuing our studies of [2+3] cycloaddition reactions involving π-deficient alkenes [1,13-17], in the present work we tested thoroughly the reaction of 1-chloro-1-nitroethene with a homogeneous series of (Z)-C-aryl-N-phenylnitrones (**2a-g**). Even though the global electrophilicity of nitroalkene **1** is much lower (ω=2.88eV [1]) than that of *gem*-dinitroethene (ω=3.56eV [13]), this alkene, unlike *gem*-dinitroethene, can be isolated as a stable compound [18-20]. Furthermore, like *gem*-dinitroethene, it has only one highly shielded reaction centre, with the other being completely de-shielded. Due to the high electrophilicity and highly varied shielding of the reaction centres, the polar nature of the cycloadditions seemed very likely. Earlier studies [1] of the reactions based on the DFT reactivity indexes [21], prompted a similar conclusion.

Cycloadditions of nitroalkene **1** with nitrones **2a-g** occur readily at room temperature [1], yielding stereoisomeric *3,4-trans-* (**3a-g**) and *3,4-cis*-2-phenyl-3-aryl-4-chloro-4-nitroisoxazolidines (**4a-g)** as the only reaction products (Scheme 1). To investigate their nature, we now: (i) performed kinetic studies of the reactions; and (ii) located critical structures on reaction pathways **A** and **B** for the model pair of substrates (**1+2a**). Knowledge of the reaction mechanism is important for stereoselective syntheses both from a practical and theoretical perspective. However, the cycloadditions in question had not previously been studied in detail [18,20,22,23].

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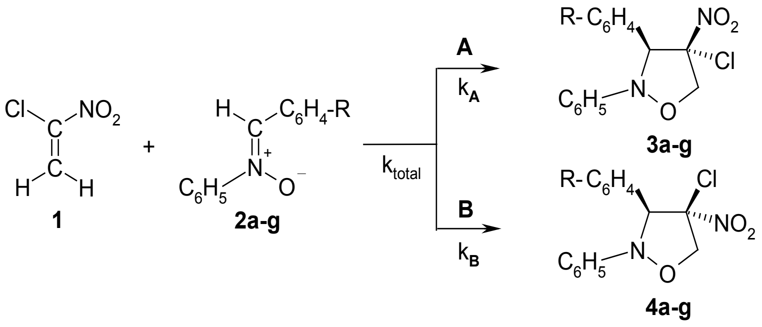
[†] Part 18 of the series 'Conjugated Nitroalkenes in Cycloaddition Reactions'; Part 17 see Ref. [1].



(**a**) R=p-CH_3O, (**b**) R=p-CH_3, (**c**) R=p-F, (d) R=p-Cl, (**e**) R=p-$COOCH_3$, (**f**) R=p-CF_3, (**g**) R=p-NO_2

Scheme 1. Reaction paths of [2+3] cycloaddition between 1-chloro-1-nitroethene **1** and (Z)-C-aryl-N-phenylnitrones **2a-g**.

2. Experimental procedure

2.1. Materials and equipment

1-Chloro-1-nitroethene **1** was prepared [24] by the dehydratation of 2-chloro-2-nitroethan-1-ol using phosphorus pentoxide at 180°C. Immediately before the reaction it was distilled twice under reduced pressure using a 12 cm Vigreux column. (Z)-C-aryl-N-phenylnitrones **2a-g** were prepared [25] by the condensation of aromatic aldehydes with phenylhydroxylamine in ethanol, and recrystallised from ethanol or hexane. Cyclohexane, p-xylene, chlorobenzene, benzene, carbon tetrachloride and chloroform (pure, POCh, Merck) were used as solvents. They were carefully purified before use according to standard procedures [26].

Kinetic experiments were carried out in a glass reactor with a thermostatically controlled jacket, magnetic stirrer, thermometer, reflux condenser and sampling device. Liquid chromatography (HPLC) was performed using a Knauer apparatus with a UV-Vis detector. A LiChrospher 18-RP 10 μm column (4×240 mm) with 70% methanol at a flow rate of 1.0 cm^3 min^{-1} as the eluent was used to monitor the reaction progress.

2.2. Kinetic procedure

The overall rate constants (k_{total}) were determined by monitoring the decrease of the HPLC peak area (A) corresponding to diarylnitrone. The kinetic experiments were carried out at 10, 20 and 30°C up to 80-85% completion. The initial concentration of nitrone was *ca.* 0.0003 mol L^{-1}, whereas nitroalkene was always used in 18-fold molar excess. In definite time intervals 250 μL samples were taken out of the reactor with a microsyringe and analyzed immediately by HPLC. It was found that for analytical band, the Bouger-Beer plot was linear within the concentration range studied. The second-order rate constants k_{total}, were obtained according to the typical method [27]. Similarly as previously [15,17], the k_{total} and values the ratio products (γ=[**3**]/[**4**]) were then applied for calculation of the rate constants k_A and k_B according to the formulas:

$$k_A = \gamma \cdot k_{total}/(\gamma+1)$$

and

$$k_B = k_{total}/(\gamma+1)$$

The results are presented in Table 1.

2.3. Quantumchemical calculations

The quantum-chemical calculations were performed on a SGI-2800 computer in the Cracow Computing Center “CYFRONET”. Hybrid B3LYP functional and 6-31G(d) basis set included within GAUSSIAN 2003 software was applied [28]. For structure optimization of the reactants and the reaction products the *Berny* algorithm [29] was applied. First-order saddle points were localized using the QST2 or TS procedures. The transition states were verified by diagonalization of the Hessian matrix and by analysis of the internal reaction coordinates (IRC). For the simulation of the solvent effect, the polarizable continuum model (PCM) [30] was applied. Calculations of critical structures were performed for the temperature T=298 K and pressure p=1atm. In presented paper the letters **LM** and **TS** denote the pre-reaction and transition complexes, respectively. A subscript is added to denote the reaction path.

3. Results and discussion

3.1. Kinetic study

We began the kinetic analysis by defining how R substituents in the nitrone phenyl ring affect the rate of cycloadditions **A** and **B** (Scheme 1). The substituent

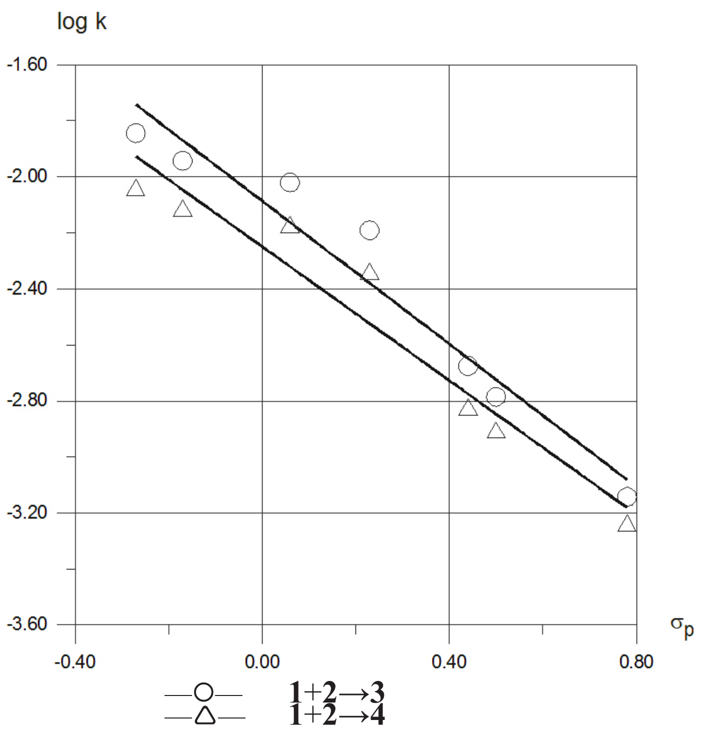


Figure 1. Plot of log k vs Hammett constants σ_p for [2+3] cycloaddition between 1-chloro-1-nitroethene 1 and (Z)-C-aryl-N-phenylnitrones **2a-g**.

effect was studied using classic correlation analysis, plotting the k_A and k_B values on the log scale (reactivity) against the values of constants σ_p, σ_R, σ_I and σ^+ [27]. Satisfactory rectilinear correlations were obtained for σ_p constants only (Fig. 1). This means that the substituent effect is transferred to the reaction centres of the 1,3-dipole, via both inductive and mesomeric effects [27]. The substituent effect on the cycloaddition rate on paths **A** and **B** is shown quantitatively by Eqs. 1 and 2.

$$\log k_A = -1.28 \cdot \sigma_p - 2.09 \qquad (R = 0.973) \qquad (1)$$

$$\log k_B = -1.20 \cdot \sigma_p - 2.24 \qquad (R = 0.968) \qquad (2)$$

The negative signs of the reaction constants ρ (slopes in Eqs. 1 and 2) suggest that charge transfer within the transition complexes of both competing reactions occurs from the nitrone substructure towards the nitroalkene substructure. It is noted that both cycloadditions are markedly influenced by substituent R. In particular, going from the least electrophilic (Z)-C-p-methoxyphenyl-N-phenylnitrone (**2a**, σ_p^R=-0.27, ω=1.48eV) to the most electrophilic (Z)-C-p-nitrophenyl-N-phenylnitrone (**2g**, σ_p^R=0.78, ω=2.88eV) the rate constants k_A and k_B are reduced by more than fifteen times. The absolute values of the ρ constants for the reactions tested are about three times lower than those which we obtained earlier for reactions of the same nitrones with E-β-nitrostyrene (ρ=-0.31 [31]). This suggests that the reactions tested here are of a much more polar nature. However, the substituent effect in reactions tested is weaker, than in typical ionic cycloadditions. For example, in the case of [2+3] cycloaddition between azometine ylides and dimethylamine propyne, rate constans for methoxy-substituted 1,3-dipole is more than twenty five times lower than in the similar reaction involving trifluormethyl-substituted 1,3-dipole [9]. As could be expected, the correlations between log k_A and log k_B and the global electrophilicity of nitrones **2a-g** are similar (Eqs. 3 and 4) (Fig. 2). However, the correlation coefficients are not so good in this case.

$$\log k_A = -0.99 \cdot \omega - 0.41 \qquad (R = 0.941) \qquad (3)$$

$$\log k_B = -0.94 \cdot \omega - 0.68 \qquad (R = 0.937) \qquad (4)$$

It should be noted at this point, that satisfactory correlations we have obtained also for plots log k_A and log k_B *versus* global nucleophilicity indexes (N [32]) (Fig. 3)

$$\log k_A = 1.40 \cdot N - 7.27 \qquad (R = 0.937) \qquad (5)$$

$$\log k_B = 1.31 \cdot N - 7.10 \qquad (R = 0.931) \qquad (6)$$

Table 1. Results of kinetic measurements for [2+3] cycloaddition between 1-chloro-1-nitroethene **1** and (Z)-C-aryl-N-phenylnitrones **2a-g**.

Nitrone					Solvent ($E_T(30)$)	t [°C]	$k_{total} \times 10^3$ [dm³ mol⁻¹ s⁻¹]	Isomer ratio γ [3]/[4]	$k_A \times 10^3$ [dm³ mol⁻¹ s⁻¹]	$k_B \times 10^3$ [dm³ mol⁻¹ s⁻¹]	R	SD
Nr	R	σ_p [27]	ω [eV]	N [eV]								
2a	CH_3O	-0.27	1.48	3.99	Cyclohexane (31.2)	20	6.69	0.51	2.26	4.43	0.999	0.01
					CCl_4 (32.5)	20	9.90	0.44	3.03	6.87	0.999	0.01
					p-Xylene (33.2)	20	9.55	0.67	3.83	5.72	0.999	0.01
					Benzene (34.5)	20	12.64	0.84	5.77	6.87	0.999	0.01
					Chlorobenzene (37.5)	20	15.58	1.05	7.98	7.60	0.999	0.02
					Chloroform (39.1)	15	17.79	1.56	10.84	6.95	0.999	0.02
					Chloroform (39.1)	20	23.52	1.56	14.33	9.19	0.999	0.01
					Chloroform (39.1)	25	34.50	1.56	21.02	13.48	0.999	0.02
					Chloroform (39.1)	30	46.57	1.56	28.38	18.19	0.999	0.01
2b	CH_3	-0.17	1.60	3.77	Chloroform (39.1)	20	19.17	1.47	11.41	7.76	0.999	0.01
2c	F	0.06	1.71	3.60	Chloroform (39.1)	20	16.30	1.41	9.54	6.76	0.999	0.01
2d	Cl	0.23	1.87	3.48	Chloroform (39.1)	20	11.04	1.40	6.44	4.60	0.999	0.01
2e	$COOCH_3$	0.44	2.11	3.26	Chloroform (39.1)	20	3.62	1.40	2.11	1.51	0.999	0.01
2f	CF_3	0.50	2.06	3.39	Chloroform (39.1)	20	2.89	1.31	1.64	1.25	0.999	0.02
2g	NO_2	0.78	2.88	2.98	Chloroform (39.1)	20	1.30	1.26	0.72	0.58	0.999	0.01

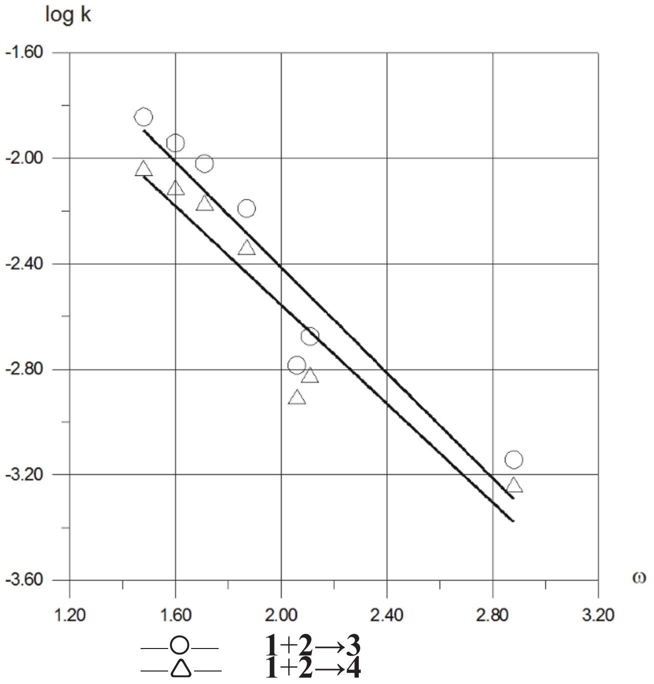


Figure 2. Plot of log k vs global electrophilicity index ω for [2+3] cycloaddition between 1-chloro-1nitroethene **1** and (Z)-C-aryl-N-phenylnitrones **2a-g**.

Good correlations log k *versus* ω and log k *versus* N confirmed, that these reaction can be considered in terms in *Domingo* terminology [21] as polar process.

Activation parameters, determined using the Eyring equation [27], for model reactions **1+2a→3a** and **1+2a→4a** provided more information about the nature of the transition complexes in the tested cycloadditions. The reactions were found to be isoenthalpic. Their activation enthalpies (ΔH≠) are 10.76 kcal mol⁻¹ and 10.75 kcal mol⁻¹, respectively, while their activation

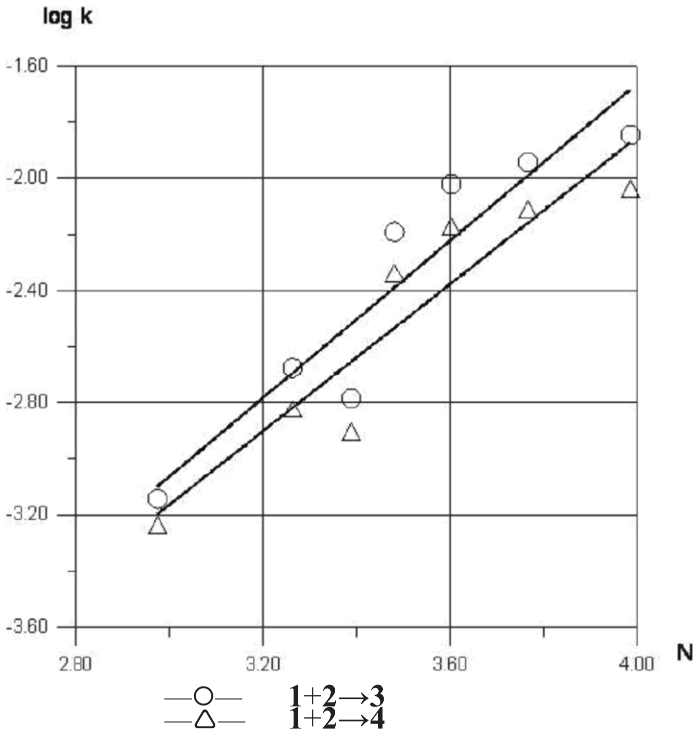


Figure 3. Plot of log k vs global nucleophilicity index N for [2+3] cycloaddition between 1-chloro-1nitroethene **1** and (Z)-C-aryl-N-phenylnitrones **2a-g**.

entropies ($\Delta S^{\neq}$) are –30.1 and –31.0 cal mol^{-1} K^{-1}, respectively.

Low values of $\Delta H^{\neq}$ contained in the range typical of the [2+3] cycloaddition of diarylnitrones to normal alkenes [2]. They harmonize with the assumption on an early transition state of the reactions [33-35], the one in which rehybrization of reacting atoms does not make much progress. High negative values of $\Delta S^{\neq}$ suggest, however, a considerable degree of ordering within the transition complexes [27], which is typical for one-step [2+3] cycloadditions [2].

Thus, the substituent effect as well as Eyring's parameters rather exclude zwitterionic mechanism of title reactions. In order to explain this problem in detail, we studied kinetics of **1+2a→3a** and **1+2a→4a** in several solvents with different ionizing power. The $E_T(30)$ values of Dimroth [36] based on the bands of solvatochromism of pyridinum-N-phenoxide betains, were used as a measure of this power. It was found (Table 1), that the rate constants k_A and k_B measured for the reaction in cyclohexane ($E_T(30)$=31.2 [37]) are lower than in chloroform ($E_T(30)$=39.1 [37]). Quantitatively the solvent effect on the cycloaddition rate was examined by plotting logk_A i logk_B *versus* $E_T(30)$ and a satisfactory linear relationships represented by the Eqs. 7 and 8 were obtained (Fig. 4).

$$\log k_A = 0.095\, E_T(30) - 5.59 \qquad (R = 0.986) \qquad (7)$$

$$\log k_B = 0.031\, E_T(30) - 3.27 \qquad (R = 0.883) \qquad (8)$$

The positive values of sensitivity indexes *a* (slopes in Eqs. 7 and 8) suggest that the transition complexes for both reactions tested are more polar than the corresponding substrates [27]. However, their low values exclude the possibility of an two-step, zwitterionic reaction mechanism. According to Domingo's classification [32,38], the reactions can be considered polar cycloadditions (PCA).

3.2. Quantum chemical exploration of reaction paths

In the part of the investigations involving [2+3] cycloadditions with the most nucleophilic nitrone **2a**, we performed quantum chemical simulations of reaction pathways **A** and **B** using a B3LYP/6-31g(d) algorithm (see Scheme 1). We have previously pursued a similar approach for the analysis of competing reaction pathways for the cycloaddition of Z-C,N-diphenylnitrone to nitroethene [14], E-β-nitrostyrene [15] and *gem*-dinitroethene [13]. We found, based on measured values of secondary kinetic isotope effects [17], that the proposed functional and the functional base correctly

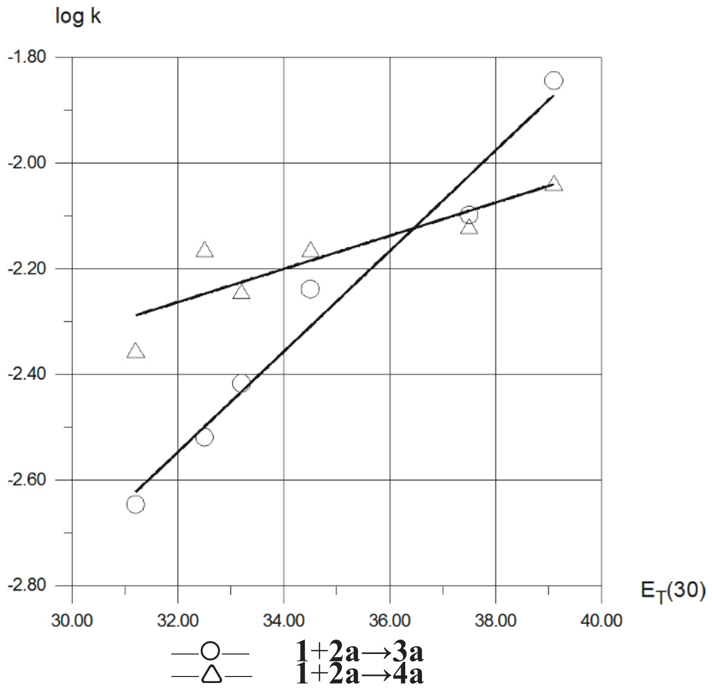


Figure 4. Plot of log k vs Dimroth $E_T(30)$ constants for [2+3] cycloaddition between 1-chloro-1-nitroethene **1** and (Z)-C-(p-methoxyphenyl)-N-phenylnitrone **2a**.

reflect the geometries of the transition complexes of polar cycloadditions. The same algorithm has successfully been used recently by other theoreticians in studies of the regioselectivity and mechanisms of [2+3] cycloadditions involving other alkenes and diarylnitrones [39-42]. In our calculations we accounted for the presence of chloroform as a dielectric reaction medium based on the PCM algorithm [30].

The enthalpy profiles of reactions **A** and **B** appear to be quite similar (Fig. 5) and has a typical shape of Curtin-Hammett principle.

Interactions between the addents on both pathways in the first stage of the reaction lead to pre-reaction complexes (**LM**$_A$ and **LM**$_B$). The transition is related to a reduction in the enthalpy of the reaction system by 0.7–1.8 kcal mol^{-1} (Table 2), and it does not require an activation barrier to be overcome. Moreover, both **LM**s are exclusively enthalpic in character, since the entropic factor ($T\Delta S$) excludes the possibility of their existence at room temperature in the form of stable intermediates (ΔG>0).

Detailed analysis of the geometries (Table 3) showed that the **LM** complexes are not orientation complexes (OC) [44]. Furthermore they are not charge-transfer (CT) complexes [45], as is proved by the degree of charge transfer (t≈0.00e) between the substructures. The oxygen atom of the nitrone substructure part (O1) in both **LM**s is oriented towards the β-carbon atom of the nitroalkene (C5). This confirms our earlier suggestions [1] that the course of the analysed reactions is controlled by the attack of the nucleophilic oxygen atom of the nitrone on the β-carbon atom of the nitroalkene.

Further movement of the reacting system along the reaction coordinate on both pathways leads to the formation of the respective transition complex (**TS**$_A$ and **TS**$_B$). The process involves an increase in the enthalpy of the reaction system by slightly more than 9 kcal mol^{-1}. Both stereoisomeric pathways are allowed from kinetic point of view ($\Delta G^{\neq}$ = 23.6 and 23.8 kcal mol^{-1} K^{-1} for pathway **A** and **B** respectively), which correlates well with the experimental data. IRC calculations confirm conclusively that the **TS**$_A$ and **TS**$_B$ structures are the only transition complexes which occur in energy profiles **A** and **B**.

In both **TS**'s form two new σ bonds. Their degree of advancement, however, is quite different (see l and Δl indexes in Table 2). The C5-O1 bond forms much more rapidly in each case, which leads to the significant asymmetry of both complexes (Fig. 6). This is quantitatively shown in the Δl index, which is defined as the difference in degrees of advancement [43] of the C5-O1 and C3-C4 bonds. The index value for the **TS**$_A$ and **TS**$_B$ structures is 0.53 (Table 2). The asymmetry of the transition complexes is accompanied by high charge transfer towards the nitroalkene substructure (Table 2). Subsequently, we have also performed optimisation of

Table 2. Eyring parameters of [2+3] cycloaddition reaction between 1-chloro-1-nitroethene **1** and (Z)-C-(p-methoxyphenyl)-N-diphenylnitrone **2a** according to B3LYP/6-31G(d) (PCM) and B3LYP/6-31+G(d) (PCM) calculations (298 K).

Transition	Theoretical level					
	B3LYP/6-31G(d)			B3LYP/6-31+G(d)		
	ΔH [kcal mol⁻¹]	ΔS [cal mol⁻¹ K⁻¹]	ΔG [kcal mol⁻¹]	ΔH [kcal mol⁻¹]	ΔS [cal mol⁻¹ K⁻¹]	ΔG [kcal mol⁻¹]
1+2a→LM$_A$	-0.7	-26.5	7.2	-1.0	-43.5	11.9
1+2a→TS$_A$	9.3	-47.9	23.6	11.5	-50.2	26.5
1+2a→3a	-9.9	-49.2	4.8	-4.6	-49.5	10.2
1+2a→LM$_B$	-1.8	-29.2	6.9	-1.3	-48.0	13.0
1+2a→TS$_B$	9.2	-49.0	23.8	11.3	-50.1	26.2
1+2a→4a	-9.5	-47.8	4.7	-4.7	-48.6	9.8

Table 3. Selected molecular properties of critical structures of [2+3] cycloaddition reaction between 1-chloro-1-nitroethene **1** and (Z)-C-(p-methoxyphenyl)-N-diphenylnitrone **2a** according to B3LYP/6-31G(d) (PCM) calculations (298 K).

Structure	C3-C4		C5-O1		Δl	μ [D]	t [e]
	r [Å]	l *)	r [Å]	l *)			
LM$_A$	4.502		2.776			7.16	0.00
TS$_A$	2.630	0.352	1.601	0.880	0.53	8.56	0.32
3a	1.596		1.429			3.47	0.12
LM$_B$	5.419		3.305				0.00
TS$_B$	2.573	0.366	1.569	0.896	0.53	8.65	0.30
4a	1.575		1.421			2.19	0.12

*) $l_{X-Y} = 1 - \frac{r^{TS}_{X-Y} - r^{P}_{X-Y}}{r^{P}_{X-Y}}$

where r^{TS}_{X-Y} is the distance between the reaction centers X and Y at the transition structure and r^{P}_{X-Y} is the same distance at the corresponding product [43].

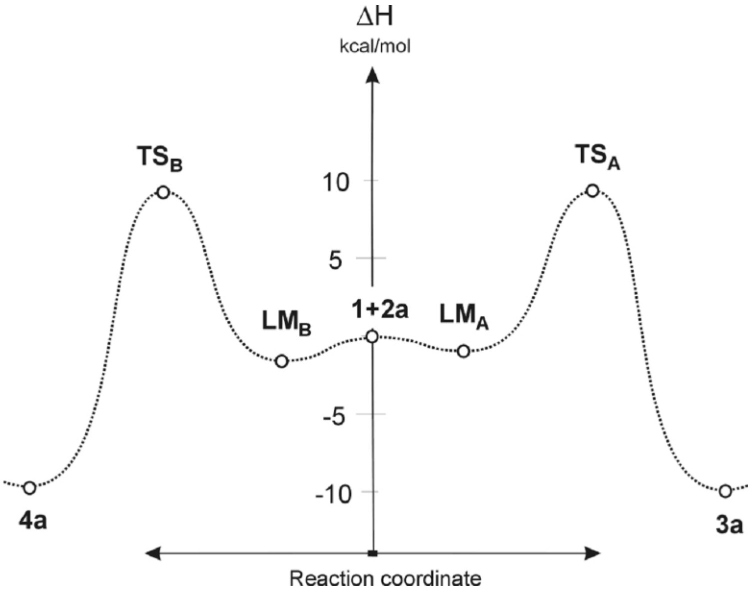


Figure 5. Enthalpy profiles for [2+3] cycloaddition reaction between 1-chloro-1-nitroethene **1** and (Z)-C-(p-methoxyphenyl)-N-phenylnitrone **2a** in chloroform according to B3LYP/6-31G(d) (PCM) calculations (298 K).

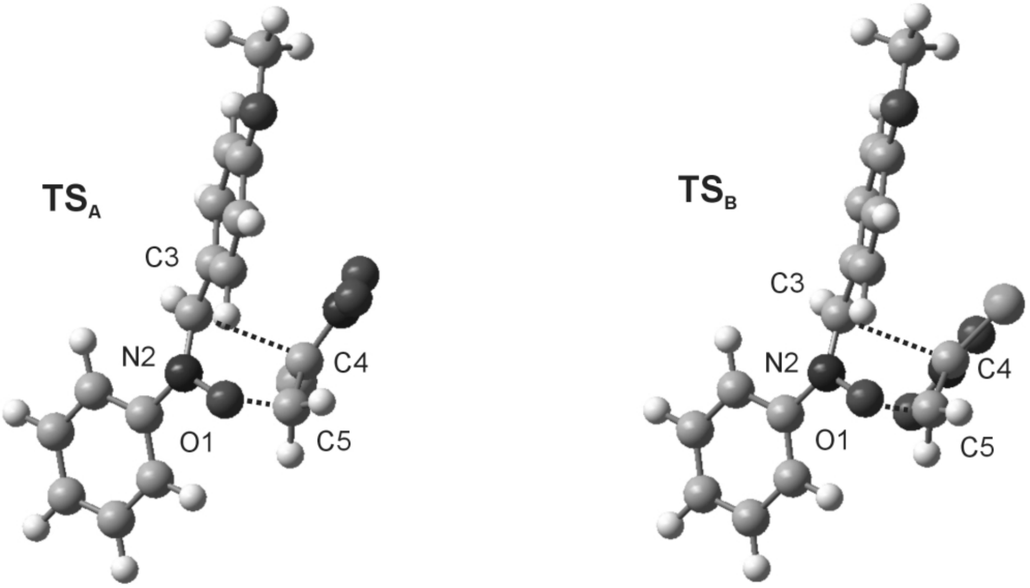


Figure 6. Views of transition complexes for [2+3] cycloaddition reaction 1-chloro-1-nitroethene **1** and (Z)-C-(p-methoxyphenyl)-N-phenylnitrone **2a** in chloroform according to B3LYP/6-31G(d) (PCM) calculations (298 K).

both **TS**s using UB3LYP functional. Results of these calculations indicate practically non-biradical nature of **TS**s (s^2<0.0000).

Therefore, B3LYP/6-31g(d) simulations confirm that the cycloaddition tested here is distinctly polar. Detailed analysis of IRC trajectories shows that, in Domingo's terminology [47], the conversion of **1+2a** into **3a** and **4a** may be considered a one-step, two-stage process, "with concomitant ring closure and without intervention of a zwitterionic intermediate". All attempts to find acyclic intermediates on the reaction paths were not successful.

Subsequently, we performed similar calculations using most advanced, B3LYP/6-31+G theoretical level. It was found, that in this case the energy profiles of pathways are qualitatively identical as for the 6-31G(d) basis set. The quantitative description of critical points only changes somewhat. In particular, the activation enthalpies calculated using the B3LYP/6-31+G(d) theoretical level are about 2 kcal mol^{-1} higher than in the case of B3LYP/6-31G(d) calculations. Also, the values of geometrical parameters of **TS**s only slightly changed.

4. Conclusion

Kinetic studies and B3LYP/6-31g(d) calculations indicate the polar nature of [2+3] cycloadditions of 1-chloro-1-nitroethene to (Z)-C-aryl-N-phenylnitrones. This is clearly confirmed by the activation parameters and the substituent and solvent effects. According to Domingo's terminology [46], detailed analysis of the energy profiles of reactions **1+2a**→**3a** and **1+2a**→**4a** leads to their classification as "one-step, two-stage" processes. A very similar description of the cycloaddition is suggested by calculations using a more advanced 6-31+G(d) basis set.

Acknowledgements

The authors acknowledge the financial support of these studies by the Polish Ministry of Science and Higher Education (grant C-2/175/DS/2012).

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