Reaction of CCl_2 with CH_2NH and the formation of dipolar and biradical ylide structures

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The potential energy surface for the reaction between CH_2NH and CCl_2 has been investigated using *ab initio* methods. We have performed geometry optimizations at the MP2/6-31G* level of theory and single point calculations at the MP4(SDQ)/6-311++G level. The reaction step for ylide formation has a free energy of activation predicted to be 5.0 kcal mol^{-1}. The parallel 1,2-cycloaddition reaction has a calculated free energy barrier of 16.5 kcal mol^{-1}, indicating that this second pathway is not competitive with ylide formation. The structure of the azomethine ylide formed in the first reaction step is similar to that found for the ylide resulting from the reaction of methylene with ammonia and corresponds to a dipolar species. This is highly unstable and rearranges to its more stable isomer, the biradical azomethine ylide, which has a structure similar to the corresponding carbonyl ylide. This species has a free energy barrier to ring closure calculated to be 21.2 kcal mol^{-1}, so it has reasonable kinetic stability. The resulting aziridine has a free energy of 24.1 kcal mol^{-1} lower than the biradical azomethine ylide, and the activation free energy of ring opening is calculated to be 45.3 kcal mol^{-1}.**

Introduction

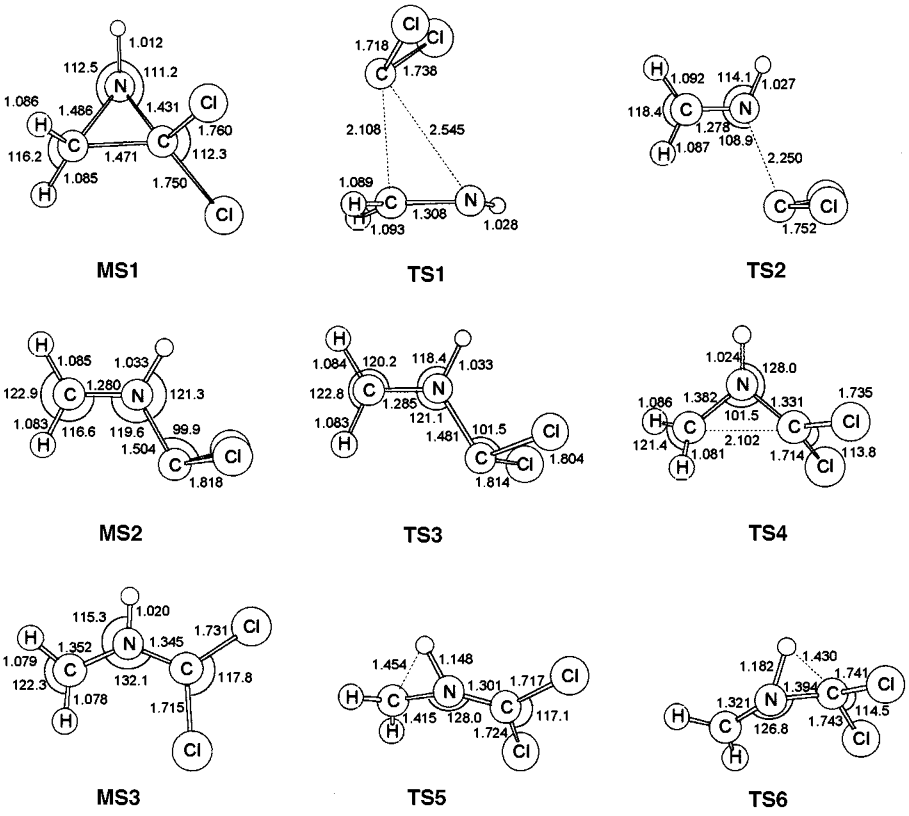
The formation of ylides of carbenes with molecules having heteroatoms with free electron pairs, *e.g.* sulfur, nitrogen and oxygen, have been studied by several researchers due to their importance in synthetic organic chemistry.[1] Nevertheless, the existence of the respective ylides is not always well established. This is especially true when the heteroatoms involved are weaker bases, such as oxygen. Some theoretical and experimental studies about the ylide formation of carbenes with water and alcohol have been reported.[2–8] An *ab initio* study by Gonzales *et al.*[2] showed that the methylene forms an ylide with water, although it is kinetically highly unstable. For the system $H_2O + CCl_2$ the situation is different. No ylide structure was found,[3] and we have showed that in this case the reaction occurs by direct insertion of the carbene in the O–H bond of the water molecule.[4] Some recent experimental studies have shown that some carbenes are able to abstract a proton from alcohols. Kirmse *et al.*[6] and Chateauneuf[7] have generated carbenes in solutions of acetonitrile and alcohol, and observed the transient spectrum of carbocations. They attributed these findings to the proton abstraction from the alcohol by the carbene, showing that the respective ylide was not formed.

For reactions of carbenes with amines or ammonia, ylides play an important role. Pople *et al.*[9] studied theoretically the $NH_3 + CH_2$ system, and they found a stable ylide structure with a stabilization energy of 28.2 kcal mol^{-1}. The ylide can rearrange to methylamine *via* proton migration, with a predicted barrier of 12.5 kcal mol^{-1}. This result is in marked contrast to that found for the ylide resulting from the reaction of H_2O with CH_2, which is considerably less stable. Experimental studies[10] of the reaction of (*p*-chlorophenyl)chlorocarbene with diethylamine allowed the formation of the ylide to be detected, and the rate constant for formation and rearrangement of this transient species was measured.

In a recent report, Naito *et al.*[11] reported a theoretical study of the competition between the Wittig and the Corey reaction mechanism for the reaction of nitrogen ($H_3N–CH_2$) and phosphorus ($H_3P–CH_2$) ylides with formaldehyde. They found that the phosphorus ylide reacts preferentially by the Wittig mechanism, while the nitrogen ylide forms a very stable complex following the Corey mechanism. The alternative Wittig reaction was not observed for the nitrogen ylide. Instead, they found a pathway that leads to 2-hydroxyethylamine. The ylide of ammonia with methylene can be characterized as a dipolar species, because there is considerable charge transfer from the ammonia to the methylene. This fact makes the nitrogen ylide a strong nucleophilic species, so it can act as an efficient agent of carbene transfer that corresponds to the Corey mechanism. A different situation occurs when the nitrogen has a double bond, as in the case of imines. In analogy to aldehydes and ketones,[12,13] imines could form ylides with biradical instead of dipolar characteristics. In this case, they could react preferentially by 1,3-cycloaddition with dipolarophiles.

The reaction of carbenes with C=O or C=N groups can follow in principle two routes: 1,2-cycloaddition, resulting in the respective epoxide or aziridine, or ylide formation. However, the possibility of the occurrence of the cycloaddition reaction is generally ignored. If this other pathway can take place, the reaction products will be different. For example, if the reaction of a carbene with a molecule having a carbonyl group occurs preferentially by 1,2-cycloaddition, the ylide formation is reduced. Therefore, this process will be less effective in reactions of 1,3-cycloaddition of the ylide with a dipolarophile. In a very recent article,[12] we have studied the $HCHO + CCl_2$ reaction using high level *ab initio* calculations, and analyzed the competition between the 1,2-cycloaddition and the ylide formation reactions. We have found that the cycloaddition is highly competitive with ylide formation, indicating that the medium and the reaction conditions have a significant influence on the resultant yields.

In the case of imines, due to the higher basicity of the nitrogen, it is probable that the ylide formation reaction is favored, so it should be the main product. Reactions of carbenes with imines were conducted experimentally, and formation of aziridines was observed.[14,15] Bartnik and Mloston[14] studied experimentally the reaction of phenylcarbene with imines, and they obtained evidence that the ylide is formed by trapping it with dipolarophiles, *e.g.* C=C, C=O and C=N groups. Also, the reactivity order found for the reaction between the dipolarophile and the ylide is C=C > C=O > C=N. In the light of these results, it seems that the mechanism for reaction of the dichlorocarbene with imines is through electrophilic attack by the carbene on the free electron pair of the nitrogen atom,



MS1 **TS1** **TS2**

MS2 **TS3** **TS4**

MS3 **TS5** **TS6**

Fig. 1 Minima (MS) and transition state (TS) structures located on the potential energy surface for the CH_2NH + CCl_2 reaction. The geometry optimizations were performed at the MP2/6-31G* level. The minimum structures are the aziridine (**MS1**), the dipolar ylide (**MS2**) and the biradical ylide (**MS3**). The structure **TS1** corresponds to transition state for reaction 1 (see Scheme 1), the structure **TS2** corresponds to transition state for reaction 2, *etc.*

forming the respective azomethine ylide. Then, this species closes the ring to form the aziridine, or it reacts with one dipolarophile to form the imidazoline derivatives.

In this work, we have studied theoretically the reaction between CCl_2 and CH_2NH, in order to determine the role played by the ylide intermediate. We have verified the possibility of the 1,2-cycloaddition reaction to compete with ylide formation, analyzed the stability of the ylide in relation to ring closure and fragmentation, and estimated the kinetic and thermodynamic properties for these reaction steps.

Calculations

In a recent study of the HCHO + CCl_2 reaction,[12] we performed goemetry optimizations at the CASSCF level in order to better describe the biradical characteristic of the resultant ylide. We observed that a SCF calculation is inadequate and leads to an unstable ylide, which dissociates into its fragments. However, the biradical characteristic of the carbonyl ylide is not accentuated, so that the restricted MP2 method was able to treat that problem and predicts a stable ylide structure. In the present study, we used the restricted MP2 method to perform geometry optimizations, employing the 6-31G* basis set. In addition, this level of theory was able to describe the kinetic isotopic effect in an elimination reaction involving an ylide of carbene with amine, thus indicating that the geometry of the transition state is accurate.[16] The MP2 approach has been found to overestimate the stability of the carbonyl ylide. So, similar behavior should be expected for the azomethine ylide, and consequently a higher level of electron correlation is required in order to predict adequate energies for the reactions involving the ylide species. We have performed MP4(SDQ) single point calculations on the MP2/6-31G* optimized geometries, using a bigger 6-311++G** basis set. All calculations were performed with the GAMESS[17] and GAUSSIAN 94[18] *ab initio* packages.

Results and discussion

Ylide structures

Nitrogen has a greater basicity than oxygen, so it can donate more effectively its free electron pair, and accentuates the electrophilic character of the CCl_2. We could predict that an azomethine ylide is more stable than the similar carbonyl ylide, and also that the former could exhibit more dipolar characteristics (greater charge transfer between the fragments), as the ylide of ammonia with CH_2, which is clearly a dipolar species. In this case, the ylide structure should be different from that observed for the ylide of formaldehyde with dichlorocarbene. In exploring the potential energy surface (PES) for the CH_2-NH + CCl_2 reaction, we have found two distinct ylide structures, which were characterized as minima by harmonic frequency analysis. These two species correspond to the structures **MS2** and **MS3** in Fig. 1, and neither of them are planar. The **MS2** structure is the dipolar species, where the donation of the electron pair from nitrogen to carbene can be seen. The **MS3** structure is the biradical species. In order to understand better the difference between these two species, we have analyzed some geometric parameters, bond orders, Mulliken charges and dipole moments. These data are given in Fig. 1 and Table 1. The length of the C_1–N and N–C_2 bonds for the dipolar ylide are very different, the first being shorter, characterizing a C=N double bond, and the second being longer than a usual single bond. The biradical ylide exhibits very similar bond lengths, with the C_1–N–C_2 angle being larger than the one for the dipolar ylide. The bond orders calculated at the MP2/6-31G* level gives support to the picture provided by the bond lengths. The C_1–N bond order in the dipolar ylide is 1.669, indicating the high character of the π bond, and the N–C_2 bond order is 0.729, which indicates that this bond is weaker than a single bond. It is interesting to compare the last value with that obtained for the NH_3–CH_2 ylide by Naito *et al.*,[11] which is

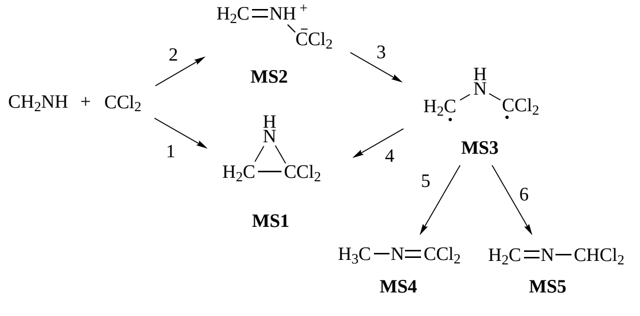
0.773. For the biradical ylide, the bond orders are 1.188 and 1.167 for the C_1–N and N–C_2 bonds, respectively. Therefore, these chemical bonds are essentially single bonds, with a small character of π bond. The Mulliken charges are presented for the carbons and for the nitrogen. These charges were also added in order to obtain the value of each fragment (CH_2NH and CCl_2). In both cases, the nitrogen has a negative charge, although it is larger in the biradical ylide. The carbons present different charges, depending on the nature of the ylide. As expected, in the dipolar ylide the C_2 carbon has a considerable negative charge, and for the biradical ylide, the negative charge on C_1 is greater than on C_2. The analysis of the charge on each fragment also revealed an interesting result. The dipolar ylide presents substantial charge transfer from CH_2NH to CCl_2 (0.435), while in the biradical ylide this charge transfer is 10 times smaller (about 0.043). The dipole moment value also indicates substantial difference between these two species. The predicted values are 7.145 D for the dipolar ylide and 2.310 D for the biradical one.

In view of the data presented above, it can be seen that the terms dipolar ylide and biradical ylide are very appropriate. The first can be seen as a species formed by a Lewis acid–base reaction, while the second can be seen as a species originating from the homolytic break of the C–C bond of the aziridine ring, so constituting a biradical species. Consequently, it can be predicted that the dipolar ylide should react with one dipolarophile by carbene transfer, as the NH_3–CH_2 ylide does,[11] and the biradical ylide should react *via* 1,3-cycloaddition, as observed by Bartnik and Mloston.[14] The reaction mechanism involving the azomethine ylides and a dipolarophile depends on the lifetime of the dipolar ylide and on the biradical ylide.

Recently, pyridine has been used for carbene trapping, generating pyridinium ylides, which show an intense absorption in the UV–VIS region.[19–21] This property was used to identify the presence of carbenes, and to measure the rate constant for the reaction of carbenes with several chemical species. Due to the similarity between imines and pyridine, we should expect analogous behavior for the reaction between carbenes and pyridine. Thus, we predict that pyridinium ylides also exist in two forms, the dipolar and biradical, the latter being the most stable and is responsible for the intense absorption of radiation.

Reaction pathways

The initial step of the $CH_2NH + CCl_2$ reaction can follow two distinct routes: ylide formation (dipolar species) or 1,2-cycloaddition. The ylide can further react *via* intramolecular rearrangement or through reaction with other species present in the medium. In this work, we are considering only the intramolecular rearrangements. The general reaction pathway is shown in Scheme 1. Each step is numbered, and all minima and transition states are indicated. In addition, Fig. 1 presents the optimized geometries of the stationary points located on the PES. The dipolar ylide (**MS2**) formed in step 2 rearranges to the biradical ylide (**MS3**). This species can follow three different paths: ring closure (step 4) forming aziridine and hydrogen migration (steps 5 and 6) forming two new imines (**MS4** and **MS5**).



Scheme 1 Possible reaction pathways for the $CH_2NH + CCl_2$ reaction

Table 1 Bond orders, Mulliken charges (q) and dipole moments (μ) for the CH_2–NH–CCl_2 ylides obtained at the MP2/6-31G* level of theory

Property	Dipolar ylide	Biradical ylide
Bond order C_1–N	1.669	1.188
Bond order N–C_2	0.729	1.167
q (C_1)	−0.077	−0.291
q (N)	−0.364	−0.432
q (C_2)	−0.213	−0.077
q (CH_2NH)	0.435	0.043
q (CCl_2)	−0.435	−0.043
μ/D	7.145	2.310

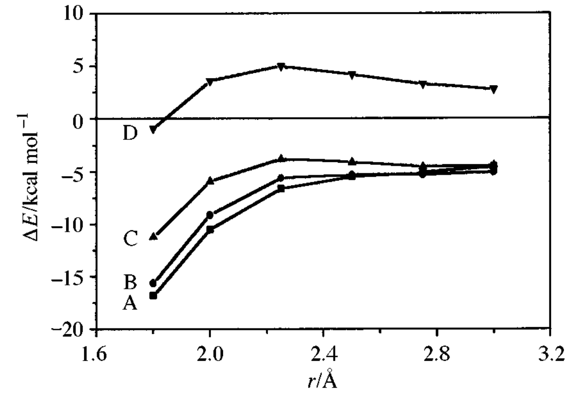


Fig. 2 Energy (relative to CH_2NH and CCl_2 fragments) as a function of the N–C_2 distance, with the other parameters optimized. A, MP2/6-31G*; B, MP2/6-311++G**; C, MP4(SDQ)/6-311++G**; D, $\Delta G^‡$.

All minima and transition states were fully optimized and characterized by harmonic frequency analysis, with the exception of step 2. At the MP2/6-31G* level, we have not found a stationary point connecting reagents and product. The addition reaction proceeds without an energy barrier. This fact can be understood from Fig. 2, which shows the energy as a function of the N–C distance, with the other geometrical parameters being optimized. Single point calculations using a more extended basis set and higher level of electron correlation show the formation of a small energy barrier below the dissociation threshold. The activation free energy $\Delta G^‡$ along the reaction path was also calculated, using the Hessian projection technique of Miller *et al.*[22] The maximum free energy of activation occurs in the maximum of the MP4(SDQ)/6-311++G**//MP2/6-31G* reaction path, so we have chosen this point as the transition state for step 2. This transition state structure is shown in Fig. 1 (**TS2**).

Table 2 presents the reaction and activation energies for the processes 1 to 6 obtained using several levels of calculation. The MP2/6-31G* level of theory overestimates the ylide stability (both structures), as occurred with the ylide of formaldehyde.[12] The MP4(SDQ) method leads to a lower stability for the ylide, and increases the barrier for steps 1 and 2. Reaction 3 has a small increase in the energy barrier, while the reactions 4, 5 and 6 present minor alterations on going from MP2/6-31G* to the MP4(SDQ)/6-311++G** level. We have also determined the thermodynamic reaction and activation parameters, and the rate constants for processes 1–4. In order to examine better the energetics of each process, we have constructed a diagram of the potential energy surface for all steps, which is shown in Fig. 3.

The formation of the dipolar ylide occurs by the attack of the vacant p orbital of the carbene on the nitrogen lone pair, as happened for the carbonyl ylide.[12] However, due to the greater basicity of the nitrogen, the transition state is symmetrical (C_s symmetry) and leads to the dipolar azomethine ylide, in contrast to the case of the carbonyl ylide where only the biradical

Table 2 Reaction and activation thermodynamic properties calculated for the reaction $CH_2NH + CCl_2$, steps 1 to 6 (Scheme 1). The standard state is 1 mol l^{-1} concentration, and $T = 298.15$ K. The geometries and frequencies were obtained at the MP2/6-31G* level. Units are in kcal mol^{-1}.

	Reaction properties					
	1	2	3	4	5	6
MP2/6-31G*	−74.0	−25.0	−21.8	−27.2	−44.5	−36.5
MP2/6-311++G**	−71.2	−24.5	−21.5	−25.2	−40.1	−33.4
MP4(SDQ)/6-311++G**	−58.4	−18.9	−13.8	−25.7	−45.3	−39.6
ΔE^{a}	−53.5	−15.4	−13.4	−24.6	−45.1	−39.0
ΔH	−55.0	−16.4	−13.5	−25.1	—	—
$-T\Delta S$	11.3	9.8	0.4	1.0	—	—
ΔG	−43.7	−6.6	−13.1	−24.1	—	—
	Activation properties					
MP2/6-31G*	2.3	−6.6	0.5	23.1	35.8	38.0
MP2/6-311++G**	1.6	−5.6	0.6	22.8	33.8	36.3
MP4(SDQ)/6-311++G**	6.1	−3.8	0.8	22.3	35.2	36.7
$\Delta E^{\ddagger a}$	7.8	−2.9	0.5	21.0	32.1	33.3
$\Delta H^{\ddagger}$	7.0	−3.3	0.1	20.8	—	—
$-T\Delta S^{\ddagger}$	9.5	8.3	1.0	0.4	—	—
$\Delta G^{\ddagger}$	16.5	5.0	1.1	21.2	—	—
$k^{b,c}$	5.0	1.3 (9)	1.9 (12)	3.5 (−3)	—	—

[a] This corresponds to MP4(SDQ)/6-311++G** energies plus the zero point energy correction using the MP2/6-31G* frequencies. [b] Rate constants in units of l mol^{-1} s^{-1}. The values in parentheses correspond to the 10 potency. [c] The value of rate constants for reactions 3 and 4 were multiplied by a factor of 2 due to the two possible pathways leading to the same product.

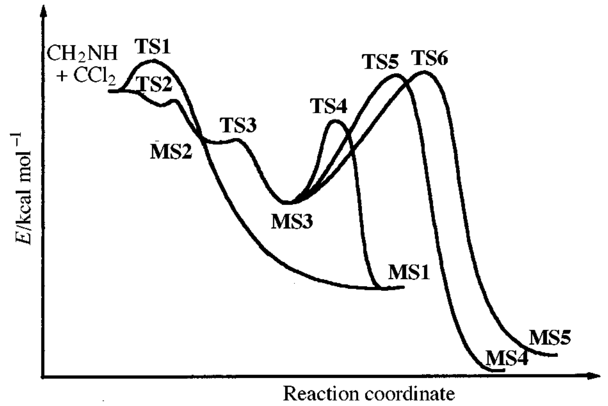


Fig. 3 Diagram of the potential energy surface [MP4(SDQ)/6-311++G**//MP2/6-31G* + ΔZPE] for the $CH_2NH + CCl_2$ reaction

species exist. Another interesting point is the negative activation energy observed for reaction 2. Consequently, the existence of a positive activation free energy is due to the decrease in the entropy. A similar situation happened in the studies of the cycloaddition of carbenes to alkenes,[23–27] where negative activation energies were observed. In addition, the cycloaddition of carbenes to alkenes is very similar to the cycloaddition of carbenes to imines, as can be observed in Fig. 1, structure **TS1**. In the present situation, due to asymmetry in the double bond, the carbene orients its vacant p orbital towards the nitrogen, which has higher electron density, and its lone pair in the sigma orbital towards the carbon center, which has a lower electron density due to the electron-withdrawing effect of the nitrogen. This reaction also has low activation energy, as observed for the reactions of some carbenes with alkenes and in the theoretical study of the addition of CCl_2 to formaldehyde.[12]

Analysis of thermodynamics and kinetics data

The formation reaction of the dipolar ylide structure has a negative activation barrier of −2.9 kcal mol^{-1}, compared with 7.8 kcal mol^{-1} predicted for the cycloaddition reaction (step 1). This difference strongly favors the reaction *via* step 2, leading to the dipolar ylide. This species is highly unstable, having an energy barrier for rearrangement to form the biradical ylide of only 0.5 kcal mol^{-1}, indicating that step 3 is very fast. The biradical ylide can follow three alternative pathways, steps 4, 5 or 6, but step 4 has an energy barrier considerably below that for steps 5 and 6. So the biradical ylide closes the ring to form the aziridine, structure **MS1**.

The free energy of activation for reaction 2 is estimated to be 5.0 kcal mol^{-1}, leading to a rate constant of 1.3 × 10^9 l mol^{-1} s^{-1}. This value is close to the diffusion limit, and it is interesting to make a comparison with the value measured for the reaction of *p*-ClPhCCl with diethylamine,[11] *i.e.* 2.33 × 10^9 l mol^{-1} s^{-1} at 27 °C. We believe that these values are similar because in the $CH_2NH + CCl_2$ reaction the dipolar ylide formed resembles that observed between amines and carbenes,[9,11] so they should have very similar transition states. On the other side, if we compare the transition state structure for the formation of the azomethine ylide (**MS2**) and the carbonyl ylide[12] from its fragments, notable structural differences can be observed. This affects the activation term ($-T\Delta S$) of these reactions. For the carbonyl ylide formation, this term is 9.8 kcal mol^{-1} (298.15 K), compared with 8.3 kcal mol^{-1} for the azomethine ylide formation. The former has a more rigid transition state. If we compare the competitive pathways, *i.e.* the 1,2-cycloaddition of CCl_2 in both cases, we will obtain very similar entropic terms, 9.4 and 9.5 kcal mol^{-1} for the reaction with HCHO and CH_2NH, respectively. Indeed, the corresponding transition states are very similar.

Reaction 3 has a free energy barrier of 1.1 kcal mol^{-1}, and the lifetime of the **MS2** species is estimated to be of the order of femtoseconds. However, due its dipolar characteristics, this species can have a longer lifetime in polar solvents, as does the $H_2O–CH_2$ ylide.[2] The biradical ylide (**MS3**) presents a relatively high kinetic stability and has a free energy barrier to conrotatory ring closure (reaction 4) predicted to be 21.2 kcal mol^{-1}. This result leads to an estimated lifetime of 5 min at 298.15 K; this time is sufficiently long to permit the ylide to be detected by spectrophotometric methods. However, it may react with other medium species reducing its lifetime and as a consequence, its detection may not be an easy task. Furthermore, our calculated MP4(SDQ) activation barrier may be overestimated.[12] The complete reverse reaction of biradical ylide formation, *i.e.* the fragmentation in $CH_2NH + CCl_2$, has an activation free energy barrier of 24.7 kcal mol^{-1}, about 3.5 kcal mol^{-1} above the ring closure reaction. These values are sufficiently high in order to lead to an irreversible ylide formation. It is interesting to compare these results with the corresponding dichlorocarbonyl ylide.[12] The latter has a lower energy barrier to ring closure, calculated to be 13.78 kcal mol^{-1}, and the fragmentation has an energy barrier of 14.49 kcal mol^{-1}, so that the carbonyl ylide formation is reversible and has a significantly shorter lifetime.

The information presented above shows that the biradical azomethine ylide (H_2C–NH–CCl_2) is thermodynamically and kinetically more stable than the respective carbonyl ylide (H_2C–O–CCl_2).[12] Also, it has a higher formation rate, and the 1,2-cycloaddition reaction does not compete with ylide formation, in contrast with the carbonyl ylide. Therefore, in principle the azomethine ylide should be more efficient than the respective carbonyl ylide in 1,3-cycloaddition reactions with a dipolarophile.

An alternative route to generate ylides is by thermal or photochemical ring opening. MacDonald and Crawford[28] achieved the thermal ring opening of 2-cyano-2,3-diphenyloxirane, and they estimated the activation and reaction energy to be 30.1 and 18–22 kcal mol^{-1}, respectively. The cyano group stabilizes the ylide in relation to the epoxide and permits rather easy ring opening of the latter one.[29] For the 2,2-dichlorooxirane, the activation free energy of ring opening is calculated to be 55.5 kcal mol^{-1}, so that in this case a significant increase in the temperature is necessary for this process to take place. Bartnik and Mloston[14] heated the *cis*-1-methyl-2,3-diphenylaziridine to 130 °C and they were able to trap the resultant ylide with a dipolarophile. The cyano group is not present in this example, so it seems that the aziridine undergoes ring opening easier than the respective carbonyl ylide. For the 2,2-dichloroaziridine, we can estimate the activation free energy of ylide formation to be 45.3 kcal mol^{-1}. The ylide is only 24.1 kcal mol^{-1} higher in energy than the aziridine, while the 2,2-dichlorooxirane is 41.7 kcal mol^{-1} more stable than the respective ylide. These data confirm the ease with which aziridine undergoes ring opening to form the azomethine ylide, compared with the analogous epoxide.

Conclusions

We have investigated the $CH_2NH + CCl_2$ reaction using *ab initio* calculations in order to determine the reaction mechanism and to estimate the respective thermodynamic and kinetic parameters of each step. Our results show that the first reaction step corresponds to formation of a dipolar azomethine ylide, with a very short lifetime. This species undergoes isomerization to a more stable biradical ylide, which is reasonably stable in kinetic terms. The ring closure reaction has an activation free energy estimated to be 21.2 kcal mol^{-1}, showing that the ylide survives for a long time at room temperature. In addition, the aziridine is more stable than the biradical ylide by just 24.6 kcal mol^{-1}, indicating a relatively easy ring opening.

Acknowledgements

This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), the Programa de Apoio ao Desenvolvimento Científico e Tecnológico (PADCT-Proc. No 62.0241/95.0) and the Pró-Reitoria de Pesquisa (PRPq-UFMG).

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Paper 7/02288C
Received 1*st April* 1997
Accepted 10*th July* 1997