Reaction of Iminopropadienones with Amines: Mechanistic Explanations of Zwitterionic Intermediate, Ketene and Ketenimine Formation

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Received: April 17, 2008; Revised Manuscript Received: July 3, 2008

The complex reaction of thermally generated iminopropadienones with amines in the gas phase and upon matrix deposition and its varying product composition is investigated using density functional theory. In the high energy gas phase addition a single amine molecule reacts readily with iminopropadienone with the decisive step being a 1,3-hydrogen shift and activation barriers of at least 100 kJ/mol. In accordance with the experiment, the formation of ketenes is favored. In the condensed phase of an amine matrix, the utilization of amine dimers both as reagents and as explicit solvents lowers the activation energy required to a feasible 20−30 kJ/mol and predicts ketenimines as the main products, as observed experimentally.

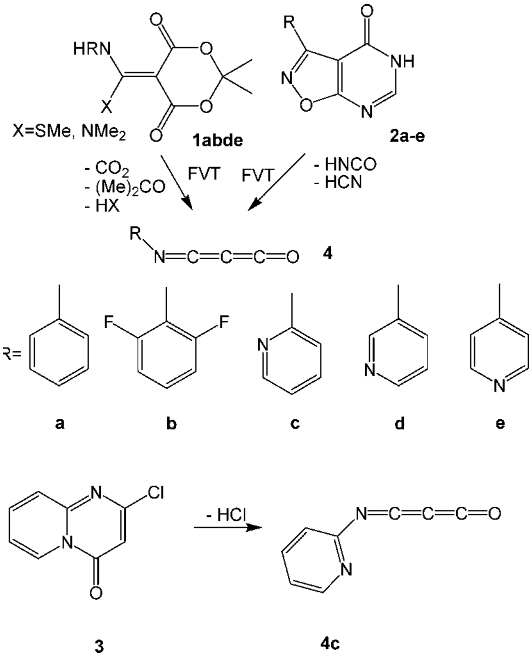
Introduction

Iminopropadienones, RN=C=C=C=O, can be generated by flash vacuum thermolysis (FVT) of 1,3-dioxane-4,6-dione (Meldrum's acid) derivatives **1**, isoxazolopyrimidinones **2**, or 2-chloropyridopyrimidinone **3**.[1−4] These unusual cumulenes have been characterized by IR and NMR spectroscopy[1−5] as well as by their chemical reactions. Iminopropadienones **4** undergo a multitude of nucleophilic addition reactions; with bisnucleophiles, cyclization leads to a variety of heterocyclic compounds containing 5-, 6-, 7-, 8-, and 9-membered rings.[2]

The C=O group in RNCCCO is expected to be more electrophilic than the C=N group and hence to react preferentially with nucleophiles. Nevertheless, the formation of both types of addition products, corresponding to the two alternate modes of nucleophile/electrophile interaction, has been described for the reactions with bisnucleophiles such as 2-aminopyridines and *N*-methylethylene-1,2-diamine.[2,4,6] Thus, in particular, the 2-pyridyl- and 2,6-difluorophenyliminopropadienones afford significant amounts of "abnormal" products apparently arising from initial attack of the strongest nucleophilic center of the bisnucleophile on the C=N group, or from attack of the weaker nucleophilic center on the C=O group.[2,4,6]

The addition of tertiary and secondary amines to aryliminopropadienones has been examined by low temperature IR spectroscopy.[7] Tertiary amines (trimethylamine) add to the C=O group to form ketenimine-type zwitterionic intermediates in all cases. Secondary amines (R'_2NH) may add to either the C=O or the C=N group to form ketenimines and ketenes, respectively.

Again, the 2,6-difluorophenyl- and 2-pyridyliminopropadienones were particularly prone to form ketenes by reaction with secondary amines on the C=O groups either in the gas phase or in matrices at ca. 100 K. 4-Pyridyliminopropadienone behaved in the same manner.



This chemistry is further complicated by the fact that the oxoketenimines **5** and imidoylketenes **6** so formed may undergo facile 1,3-shifts of the amino groups with activation barriers of ca. 62 kJ/mol in the gas phase, and 45−50 kJ/mol in polar solution (acetonitrile).[8] Because of this very facile reaction, the observation of ketene and/or ketenimine formation in *gas phase* reactions at elevated temperatures does not necessarily provide a clear picture of where the initial attack of the amine takes place. To answer this question, it was necessary to examine the reactions in low temperature matrices.[7]

In an effort to shed light on the reactivities of iminopropadienones in amine addition reactions, we have examined this reaction computationally and report the results herein.

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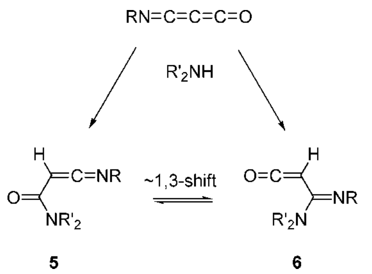
10.1021/jp803352m CCC: $40.75



Computational Methodology

All calculations were performed with the program package Gaussian 03.[9] Density functional theory (DFT) with the B3LYP functional[10,11] together with Pople's 6-311++G(d,p)[12-14] basis set was used as the default level of theory. It has proven itself as a reliable approach in the study of related systems.[15] The triple-ξ basis set with diffuse functions is necessary to correctly treat the weak interactions in the intermediate zwitterions and other complexes. The nature of all stationary points as true minima or as first-order transition states was confirmed by calculating harmonic frequencies. Scaled zero-point vibrational energy corrections have also been taken into account.[16] Additionally, the influence of an amine matrix environment was modeled by employing the PCM SCRF[17] approach with ether as solvent. It is structurally related to the amines used here with a similar dielectrical constant ϵ of 4.335 (dimethylamine (6.3), diethylamine (3.7)).

Results and Discussion

To understand the complexity of the reaction, the experimental observations for the addition of dialkylamines to iminopropadienones in low temperature matrices (ca. 50−200 K) are summarized in Table 1. The first IR-spectroscopic data obtained immediately upon deposition of the iminopropadienone−amine mixture on the coldfinger of the cryostat indicate that there is some reaction taking place already in the gas phase, at least for some of the investigated iminopropadienones.

Several conclusions can be drawn from these data: a gas phase reaction preceding deposition usually leads to ketene formation (**6**), often accompanied by some ketenimine. In our previous study, we have concluded that the zwitterions observed in the low temperature matrix reactions are due to an amine addition at the more electrophilic C=O end of the molecule.[7] Ketenimine **5** can always be found as the product, together with varying amounts of ketene **6** in the matrix reactions. One additional remark: if a product or particularly a zwitterionic intermediate is not observed, it does not necessarily mean that it is not formed; it may not be kinetically or thermodynamically stable under the reaction conditions.

In a first step, we have simulated the reaction that can take place immediately after generation of the iminopropadienone under thermal conditions in the gas phase. There are two main pathways for the addition of a monomeric amine (dimethylamine is used herein) to iminopropadienone, which are presented in Figure 1, and the results are given in Table 2. The monomeric nature of the amine at the high temperatures available under FVT conditions (generally around 500−700 °C) has been confirmed by calculation of the free energy of the dimerization energy of dimethyl amine: the H-bonded dimer may exist at very low temperature ($\Delta H = -6.7$ kJ/mol); however, the entropy effect is large [−104 J/(mol K)] and the dimer is predicted to be no longer favorable in the gas phase above 60−80 K.[18]

TABLE 1: Products Observed Experimentally in Low Temperature Matrices and Resulting from Addition of Dialkylamines to 4 (Minor Products in Parentheses)

compound	gas phase reaction	zwitterion formation[a]	matrix reaction
4a (R = phenyl)	**5**	2109 cm^{-1}	**5**
4b (R = 2,6-difluorophenyl)	**6** (+ **5**)	2113 cm^{-1}	**5** (+ **6**)
4c (R = 2-pyridyl)	**6** (+ **5**)		**6** (+ **5**)
4d (R = 3-pyridyl)	**6** + **5**	2116 cm^{-1}	**6** + **5**
4e (R = 4-pyridyl)	**6** (+ **5**)	2113 cm^{-1}	**6** + **5**

[a] Observed frequencies.

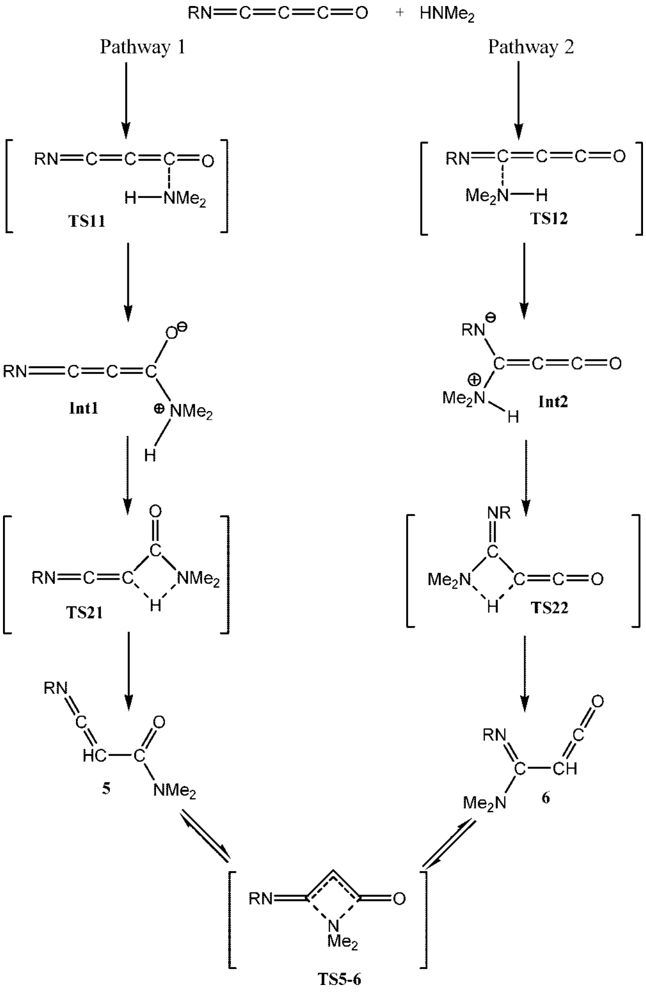


Figure 1. Addition pathways for the reaction of dimethyl amine with iminopropadienone.

TABLE 2: Relative Energies (kJ/mol; B3LYP/6-311++G(d,p) + ZPVE) of Structures in Pathways 1 and 2 of Dimethylamine Addition to Iminopropadienones, Relative to Reactants (4 + Amine)

compound	TS11	Int1	TS21	5	TS12	Int2	TS22	6	TS5−6
4a	–	–	130	−88	50	49	109	−49	0
4b	–	–	127	−85	51	39	100	−64	−6
4c	–	–	129	−91	43	41	104	−56	−2
4d	–	–	127	−91	43	39	103	−55	−2
4e	–	–	126	−90	44	40	102	−61	−5

Although the occurrence of zwitterionic species in the addition of amines to related systems is well-known,[19] the formation of zwitterions is not favorable in the gas phase reaction of RNCCCO with a single amine molecule. Neither the transition

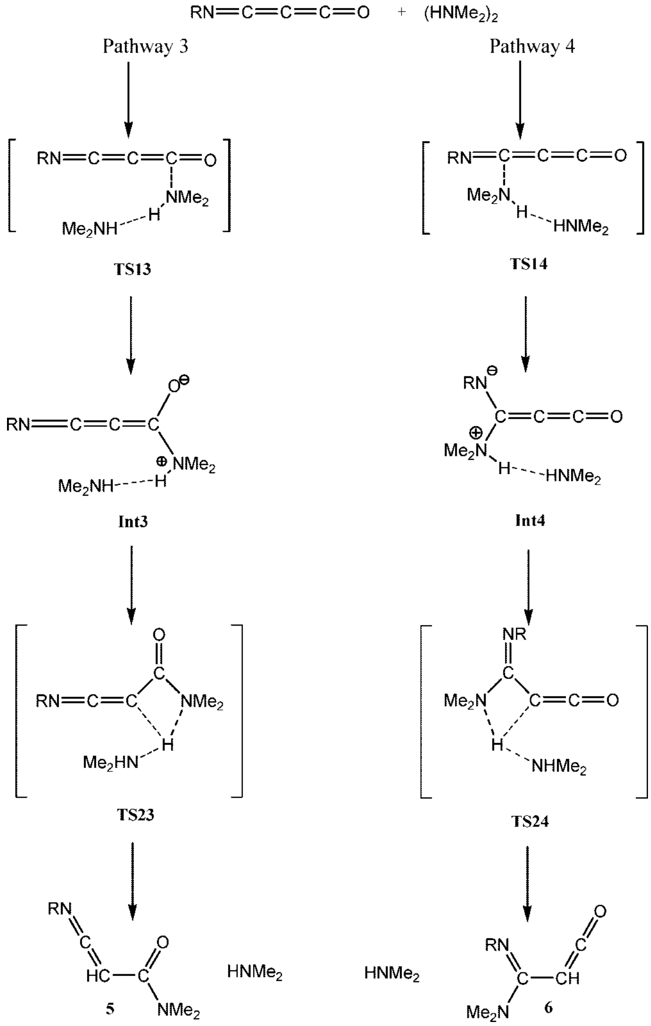


Figure 2. Addition pathways for the reaction of a dimethyl amine dimer with iminopropadienone.

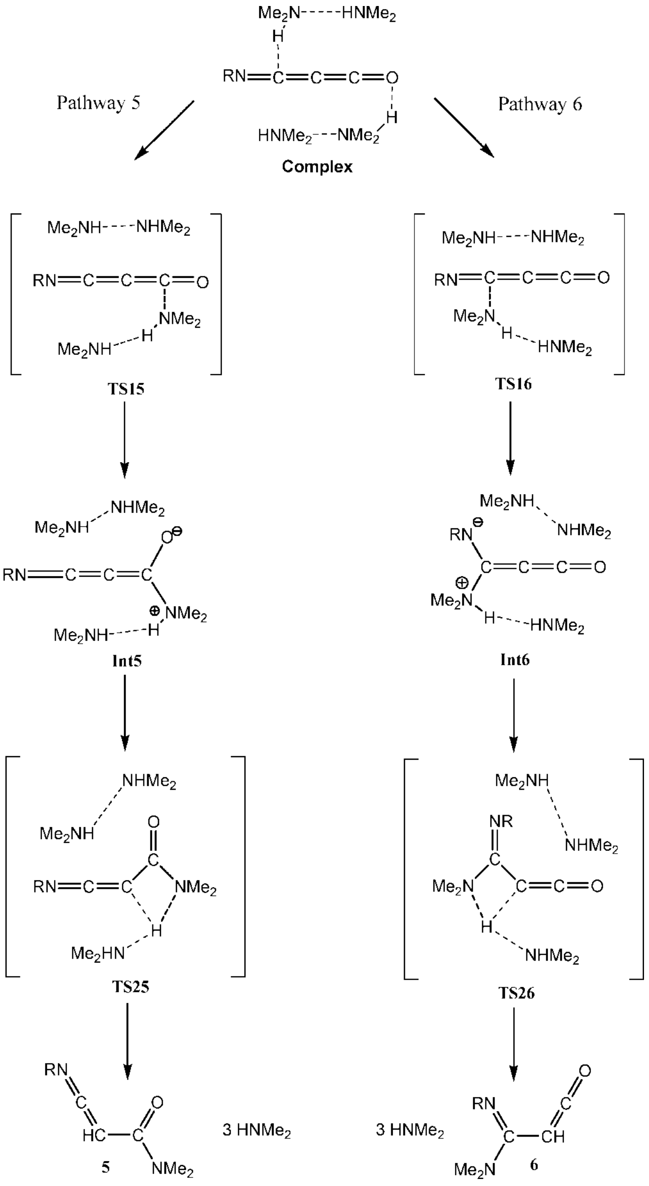


Figure 3. Addition pathways for the reaction of a dimethyl amine dimer with iminopropadienone, assisted by an additional amine dimer.

state for formation of the initial C−N bond nor the adduct itself could be located for the substituents in pathway 1, indicating that the zwitterion **Int1** is not sufficiently stabilized in the gas phase at the given level of theory.[20] In contrast, for pathway 2 the zwitterions could be located, with an activation barrier of 43−51 kJ/mol for formation, but a stabilization of only 1−12 kJ/mol relative to **TS12**. Possible prereaction complexes between an amine and an iminopropadienone are not considered for this mechanism, mainly because the overall reaction barriers are significantly larger than stabilization by van der Waals adducts, which easily revert to separate molecules under the given conditions.

The highest energy step in the addition of a single amine is the 1,3-hydrogen transfer step (**TS2**), converting the intermediate zwitterion to the product heterocumulene. The average barrier for all substituents of 128 kJ/mol for ketenimine formation (pathway 1) compared to 103 kJ/mol for ketene formation indicates that the latter is generated somewhat more easily. This is in agreement with the observation that there is sometimes a preference for ketene formation in FVT/matrix isolation experiments. However, the 1,3-shift of an amino group (**TS5**−**6**), converting the ketene to a ketenimine, is hindered by only about 50 kJ/mol; the reverse reaction requires some additional 20−40 kJ/mol due to the higher thermodynamic stability of **5**. Therefore, the nature of the product isolated in the matrix depends on the relative thermodynamic stabilities of **5** and **6**, and one should always expect to see a large excess of ketenimine **5**. Because this is not always the case under mild FVT conditions, the conclusion drawn from both the experimental observations and the calculated data is that a thermodynamic equilibrium is not reached prior to deposition. Hence ketenimine formation in the gas phase can be due to a nonequilibrium ketene−ketenimine conversion. This is due to the short contact time and low collision number in FVT. The fact that the amounts of ketene observed are very high in cases **b**−**e** indicates that the ketenes are formed first, in accordance with the lower activation barriers for their formation.

There are two major problems with the “single amine mechanism” as described above (addition of a single monomeric amine molecule to the iminopropadienone, Figure 1) with regard to the experimental matrix reactions. First, it does not satisfactorily explain the observed preference for ketenimine formation in matrixes, and more importantly, the activation barriers (**TS2**) that need to be overcome are much too high for a reaction to take place in the matrix. But this is exactly what happens! So there must be a significant change in the reaction mechanism

TABLE 3: Relative Energies (kJ/mol; PCM-B3LYP/6-311++G(d,p) + ZPVE// B3LYP/6-311++G(d,p) of Structures in Pathways 3 and 4 of Dimethylamine Addition to Iminopropadienones, Relative to Reactants (4 + Two Amine)[a]

compound	TS13	Int3	TS23	5	TS14	Int4	TS24	6
4a	24 (12)	14 (13)	24 (33)	−91 (−88)	38 (23)	8 (7)	16 (24)	−46 (−49)
4b	18 (7)	8 (8)	16 (24)	−91 (−85)	38 (24)	−3 (0)	−3 (5)	−63 (−64)
4c	18 (4)	0 (−1)	6 (16)	−91 (−91)	33 (16)	0 (−1)	6 (16)	−56 (−56)
4d	18 (5)	5 (5)	13 (23)	−90 (−91)	33 (17)	−3 (−4)	5 (14)	−56 (−56)
4e	16 (3)	1 (3)	8 (20)	−91 (−90)	32 (17)	−4 (−3)	1 (12)	−62 (−61)

[a] Numbers in parentheses are for the gas phase reactions.

TABLE 4: Relative Energies (kJ/mol; PCM-B3LYP/6-311++G(d,p) + ZPVE// B3LYP/6-311++G(d,p)) of Structures in Pathways 5 and 6 of Dimethylamine Addition to Iminopropadienones, Relative to Reactants (4 + Four Amines)

compound	complex	TS15	Int5	TS25	5	TS16	Int6	TS26	6
4a	9 (−30)	27 (−8)	16 (−10)	26 (8)	−91 (−88)	54 (26)	−25 (2)	16 (−6)	−46 (−49)
4b	4 (−28)	19 (−11)	6 (−14)	14 (0)	−91 (−85)	43 (13)	−9 (−33)	*a*	−63 (−64)
4c	6 (−38)	20 (−18)	7 (−20)	15 (−8)	−91(−91)	41 (3)	−6 (−32)	*a*	−56 (−56)
4d	6 (−34)	19 (−17)	5 (−20)	14 (−3)	−90(−91)	49 (21)	−9 (−35)	*a*	−56 (−56)
4e	6 (−32)	17 (−16)	1 (−20)	10 (−5)	−91(−90)	44 (17)	−11 (−35)	*a*	−62 (−61)

[a] Not located. Numbers in parentheses are for the gas phase reactions.

after deposition of the reactants. As we are now dealing with a condensed phase of mostly amine, it seems justifiable to include a solvent field into the calculation. Also, one needs to consider amine oligomers (in our case a dimer; see Figure 2 and Table 3), because the high concentration and low temperature strongly favor their existence in a matrix. Furthermore, amine dimer formation has been invoked in the interpretation of other matrix reactions.[21]

It can be seen that the inclusion of the second amine leads to a mechanism without a high energy 1,3-hydrogen shift. Instead the hydrogen atom is transferred to the second amine (**TS2x**) and the same hydrogen is subsequently attached to the backbone carbon atom (the latter step proceeds without an energy barrier; i.e., no stationary points were located).[22] One should point out that the assistance of the second amine in the hydrogen transfer can be seen as the beginning of a cooperative effect,[23] similar to that used to explain the catalytic effect of water ice molecules.[24] In addition, tunneling of the hydrogen atom is a possibility, and the two effects together suggest that the hydrogen transfer may be essentially barrierless. The barrier of the initial addition, which has now become the decisive step in the mechanism, is also significantly reduced by the second amine, to the point where reactions may be expected in the low-temperature matrix. The application of the solvent field increases the activation energy for the initial addition and lowers the barrier for the hydrogen transfer (**TS23** and **TS24**) at the same rate for all substituents. All reactions should now lead to ketenimine formation in the matrices, in agreement with observations. Furthermore, this confirms the observation of the formation of zwitterions attributed to amine addition to the C═O end of the molecules in the previous study.[7]

However, the mechanism does not explain why also ketenes are observed in some of the matrix reactions. Therefore, this model needs to be refined to take into account the neighboring effect of the dimethylamine matrix. Figure 3 describes a mechanism similar to the one in Figure 2 but includes another dimethylamine dimer stabilizing the intermediate structures by additional hydrogen bonds to both iminopropadienone and the first dimer, therefore mainly acting as explicit solvent molecules. Additionally, prereaction complexes between iminopropadienone and the amine dimers, which can also be found in the simpler models, are now discussed. The results are summarized in Table 4.

Before an attacking amine (dimer) will react with an iminopropadienone, it will form weak van der Waals or hydrogen bonded prereactive complexes. In the gas phase calculations, these complexes are stabilized by about 30 kJ/mol relative to the reactants (with 4 separate amines) but become slightly unfavorably in the simulated solvent environment. No influence on the nature of the iminopropadienone is observed. The same conclusion is reached for the second mechanism discussed above (addition of one amine dimer).

The inclusion of a solvent field again leads to a relative stabilization of the intermediates compared to the first transition states, which is not surprising given their more pronounced zwitterionic nature. The C−N bond formations are the steps with the highest activation energies and therefore the rate limiting steps (**TS15** and **TS16**). These barriers are low enough to allow reactions to take place even in low temperature matrixes. The hydrogen transfer from the first to the second dimethylamine molecule requires activation energies well below those for the initial attack in case of the C═O addition, which leads to ketenimine formation (**TS25**). For the C═N addition leading to ketenes, no second transition states **TS26** corresponding to a hydrogen transfer could be located except in the case of **4a**; all attempts lead to rearranged transition structures that are well below the intermediates **Int6** in energy, so that one can assume that these subsequent H transfer steps are not decisive. The hydrogen transfer to the cumulenic carbon atom again appears to be without a notable barrier, thereby following the same trends as described for the model with two amine molecules above (Figure 2, Table 3).

The occurrence of ketenimine as a product in all cases can be explained from the data in Table 4: pathway 5, which yields **5**, is calculated to have a significantly lower barrier (17−27 kJ/mol) compared to pathway 6 (ketene formation, 41−54 kJ/mol). Furthermore, Table 4 gives an indication why ketene **6** is observed as a second product in case of the difluorophenyl-, 2-pyridyl- and 4-pyridyliminopropadienones (**4b**, **4c**, **4e**): the activation energies for pathway 6 leading to ketenes is somewhat lower relative to those of **4a** and **4d** in these cases, thus tending toward the experimental results, although the difference in activation barriers of only about 10 kJ/mol is small.

One notable observation is the fact that reaction of the fluorinated iminopropadienone **4b** gives an unusually high proportion of ketene **6b**,[7] although the ketenimine still domi-

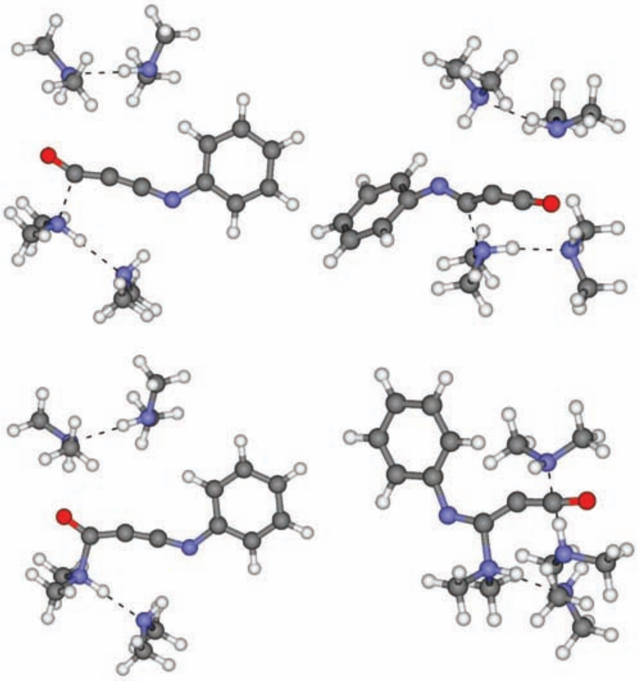


Figure 4. Optimized first transition states **TS15** (top left) and **TS16** (top right) and zwitterions **Int5** (bottom left) and **Int6** (bottom right).

nates.[25] This appears to be a common phenomenon when using fluorinated aryl substituents, which lead to particularly stable fluorinated ketenes. Special stability has also been found in other fluorinated ketenes.[26] This "fluorine effect" is confirmed in Tables 2 and 4 for the difluorophenyl compounds '**b**'.

So, in summary, this model, using an amine dimer to facilitate the reaction and another dimer to stabilize intermediate structures, helps to explain the observed experimental results for the reactions of iminopropadienones **4** in amine matrixes.

One note about the number of amines: the system of four amine molecules is a minimal model for the description of the reaction of iminopropadienones in an amine matrix at low temperatures. In a matrix, iminopropadienones will be embedded in many more amine molecules, which will be stabilizing the intermediate structures (Figure 4) even more with hydrogen bonds. During the course of this study, we have found several alternative structures of similar energy to the ones presented herein, particularly for the hydrogen relay from the first amine molecule to the carbon backbone.[27] Therefore, additional amine molecules should facilitate this part of the reaction even more, so that a barrierless transfer may in fact be plausible. In all cases, the rate determining step is the initial formation of a bond between the attacking amine nitrogen atom and the C=N or C=O carbon atom.[28]

Conclusion

The complex reaction of thermally generated iminopropadienones with amines in the gas phase and upon matrix deposition and its varying product composition cannot be described by a single reaction mechanism. In the high energy gas phase reaction an amine molecule reacts readily with iminopropadienones **4** with the decisive step being a 1,3-hydrogen shift and activation barriers of at least 100 kJ/mol. Here, the formation of ketenes is favored, as also observed experimentally. In the low temperature condensed phase of an amine matrix, the utilization of amine dimers both as reagents and as explicit solvents not only lowers the energy required to a feasible 20−30 kJ/mol but also predicts the correct product and indicates differences in the reactivity of the variously substituted iminopropadienones. Although our best model using four molecules of the amine may be an oversimplification, it nevertheless gives much needed insight into the details of these addition reactions.

Acknowledgment. Financial support by the DFG and generous allocation of computing time at the CSC, Uni Oldenburg is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and total energies for all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) These findings are confirmed by calculations at several additional levels of theory: neither the improvement of electron correlation nor the combination with larger (or smaller) basis sets led to the localization of the missing transition state and zwitterion. However, gas phase calculations at the HF/6-31G(d) level yield these structures, which are also found when including a simulated solvent field in DFT optimizations.

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(22) Attempts to locate stationary points after passing through **TS2(3,4)** including IRC calculations only lead to structures resembling a complex between the final product and dimethyl amine. Partial optimizations gave intermediate structures that lie much lower in energy compared to **TS2(3,4)**, thereby justifying the assumption that the process is barrierless. Additionally, six-membered ring transition state similar to those proposed by Tidwell[21] could not be located at various levels of theory.

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(24) (a) Tordini, F.; Bencini, A.; Bruschi, M.; De Gioia, L.; Zampella, G.; Fantucci, P. *J. Phys. Chem. A* **2003**, *107*, 1188. (b) Duvernay, F.; Chiavassa, T.; Borget, F.; Aycard, J.-P. J. *Am. Chem. Soc.* **2004**, *126*, 7772. (c) Duvernay, F.; Chiavassa, T.; Borget, F.; Aycard, J.-P. *J. Phys. Chem. A* **2005**, *109*, 603.

(25) In numerous experiments on the imidoylketene−oxoketenimine rearrangement (using FVT of Meldrum's acid derivatives with 5-[(arylamino)(methoxy)methylene] substituents), a predominance of the ketenimine over the ketene is always seen, as expected. Fulloon, B. E.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 1363. The proportion of the ketene is particularly high when fluorinated aryl substituents are used (i.e., in the equilibrium between $F_n{-}Ar{-}N{=}C{=}C(H){-}CO{-}OMe$ and $F_n{-}Ar{-}N{=}C(OMe)CH{=}C{=}O$), most dramatically with pentafluorophenyl (Fulloon, B. E. *Ph.D. Thesis*, The University of Queensland, Brisbane, **1997**,).

(26) Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1218, and references therein.

(27) Only the most consistent data, i.e., similar geometrical arrangement, number of coordinations and a complete (reactant to product) sequence, is presented herein. They represent also the pathways that possess the lowest overall energy. There are individual structures that lie lower in energy than the respective ones presented but no connection to the overall process could be found.

(28) For the complete mechanism, only the initial addition to a double bond is important and subsequent hydrogen relay is not. For each of these first transition states, only two different structures could be located and the one presented is significantly lower in energy.

JP803352M