Necessity to consider a three-water chain in modelling the hydration of ketene imines and carbodiimides

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A theoretical study of the hydration of a model ketene imine (R_2C=C=NH) and carbodiimide (RN=C=NR) has been undertaken. The detailed hydration mechanism of the simplest cumulenes by water and water clusters (HX=C=NH + n $H_2O \rightarrow H_2XCONH_2$ + (n − 1) H_2O, n = 1, 2, 3 and X = CH, N) was modelled using high-level *ab initio* MO methods. Geometric and energetic parameters were determined for two possible reaction channels involving water attack across both C=C and C=N bonds of ketene imine. Using one and two actively participating water molecules to model the hydration, calculated results consistently show that the C=N addition, giving first an amide enol, is favoured over the C=C yielding immediately the amide product. A reverse situation occurs when a chain of three water molecules is used. Since attack in two different planes is possible in the latter case, reducing the unfavourable distortion of the methylene group, the C=C addition becomes easier to perform than the C=N, with an energy barrier of 48 kJ mol^{-1} found at the CCSD(T)/6-31G(d,p) level, the lowest barrier of all the calculated water chain models. These findings are consistent with experimental evidence for direct formation of C=C products in non-hindered ketene imines. Thus, water oligomers higher than the dimer seem to make a primordial contribution to the rate of the hydration and are really needed to perform a concerted reaction. These gas-phase results are confirmed when the effect of the solvent bulk is taken into account in PCM calculations. Hydration of the analogous carbodiimide, in which addition can only occur across the C=N bond, was also studied. The C=N addition with the aid of a three-water cluster is rate-determining followed by a tautomerization of the primary adduct leading to urea. Carbodiimide hydration turns out to be easier to achieve than ketenimine hydration.

Introduction

Although ketene imines were first reported by Staudinger in 1921,[1] much of the knowledge of this functional group has been accumulated within the last twenty years or so. Ketene imines belong to the general class of hetero-cumulenes (Y=C=X) and are, in general, highly reactive and undergo both electrophilic and nucleophilic additions, together with cycloaddition reactions.[2]

Kinetic studies[3] showed that in aqueous solution, the hydration of phenyl- and diphenylketene imines is dominated by rate-determining proton transfer to the β-carbon. The preferred carbon site is supported by *ab initio* MO calculations[4,5] on the protonation of the parent ketene imine CH_2=C=NH. In fact, the corresponding CH_3-C≡NH^+ is by far the most stable protonated form, as compared with other possible forms CH_2=C=$NH_2{}^+$ or CH_2=CH=NH^+. Therefore, only the possibility of proton transfer to the β-carbon upon attack of water and water dimer across the C=C bond of ketene imine was studied in earlier theoretical work.[6,7] However, Hegarty *et al.*[8] have recently performed experiments in which conditions were generated in such a way that ketene imine could undergo *N*-protonation as well. When using very hindered ketene imine, an amide enol (**a**) has been positively identified as a reaction intermediate which subsequently dissociates forming a ketene plus an amine as final products [eqn. (1)].

$$R_2C{=}C{=}NR + H_2O \longrightarrow R_2C{=}COH(NHR) \longrightarrow R_2C{=}C{=}O + NH_2R \quad (1)$$

Such a change in the protonation site from the normal carbon was ascribed to the steric crowding around the β-carbon. On the other hand, the hydration and alcoholysis of isocyanates (RN=C=O) have been found to occur at the C=N moiety.[9] It seems therefore necessary to investigate both possibilities of water attack across the C=C (concerted mechanism) and C=N (two-step reaction) bonds of ketene imine.

In the present paper, both types of attack are studied in considering different numbers of active water molecules. The apparent ease with which the hydration occurs is confirmed to be due to the water chain intervention in the proton transfer process; more particularly, it is shown that at least three water molecules are needed to perform the hydration of ketene imine in a concerted manner. For the purpose of comparison, the hydration of the parent carbodiimide (HN=C=NH), in which only a C=N addition is possible but for which the mechanism has not been as thoroughly investigated as that of other cumulenes,[9] is also investigated.

Details of calculation

Ab initio molecular orbital calculations were carried out using the GAUSSIAN94[10] set of programs. The stationary points of interest were initially located and characterized by harmonic vibrational analyses employing analytical energy hessians at the Hartree–Fock (HF) level with the dp-polarized 6-31G(d,p) basis set. The relevant equilibrium and transition (TS) structures were then re-optimized at second-order Møller–Plesset perturbation theory (MP2) level with the same basis set. Improved relative energies between stationary points were finally estimated using single-point electronic energies with the quadratic configuration interaction (QCISD(T)) and coupled cluster (CCSD(T)) methods that include all the single and double excitations plus perturbative corrections for connected triple excitations, and MP2/6-31G(d,p) optimized geometries. These values were further corrected for zero-point vibrational energies (ZPE). In the correlation treatments, all core orbitals were kept frozen. The effect of solvent bulk on the different

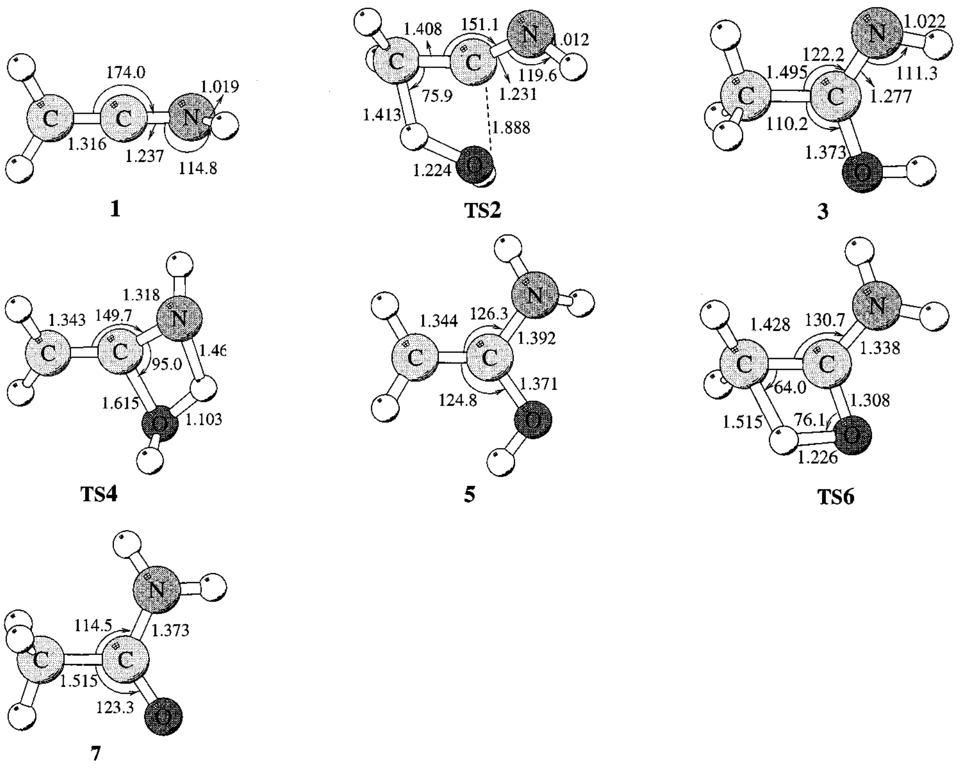


Fig. 1 MP2/6-31G(d,p) optimized structures of stationary points along the hydration path of ketene imine with one water molecule ($H_2C=C=NH + H_2O$) across both C=C and C=N bonds.

processes is simulated employing the continuum approach in which the solvent is considered as a dielectric continuum. A polarizable continuum model (PCM),[11] in which the electrostatic influence of the whole solvent bulk is taken into account, has been used in this work. Throughout this paper, bond lengths are given in angströms, bond angles in degrees, zero-point vibrational (ZPE) and relative energies, unless otherwise mentioned, in kJ mol^{-1}.

Results and discussion

As stated above, the objectives of the present study are the following: (i) the possibility of water addition across the C=N bond of ketene imine; (ii) the efficiency of an increasingly larger water cluster in the proton transfer; (iii) the influence of the solvent bulk on the reaction process; and (iv) a comparison of the hydration of ketene imine with that of carbodiimide.

The calculations were carried out at the highest levels of theory presently available to us. For processes termed "gas phase", the level of theory employed is MP2/6-31G(d,p) for the geometry optimization of stationary points and CCSD(T)/6-31G(d,p) for energetic parameters. In the following discussion, the bond lengths and bond angles shown refer to the MP2 values (Fig. 1, 2 and 3) whereas energies quoted refer to the CCSD(T) results (*cf.* Table 4, column 6). In the following discussion, we consider only the enthalpic terms. It is obvious that in the compact and ordered TS's such as those described hereafter, the entropic terms are expected to be negative and important. Nevertheless, a difficulty arises from the choice of points of reference. The water chains could in fact be regarded either as separated molecules or as water clusters (dimers or trimers). In addition, pre-association complexes involving the cumulene and a water cluster could, in some cases, be formed. In the latter cases, while the enthalpies of complex formation are quite small, the entropic counterparts are quite large. In view of the many possible references, it is not always possible to be consistent in estimating the entropic contributions and thereby the free energies of activation, in going from a small to a larger multi-molecular system. Therefore we would prefer to consider only the enthalpic terms of the activation parameters, whose computed values are more consistent with each other.

Hydration of ketene imine

There have been several experimental[12,13] and theoretical[4,5,14] studies on the parent ($H_2C=C=NH$) species; therefore its structure and stability warrant no further comment. Although earlier theoretical studies[6,7] have made use of low-level *ab initio* MO calculations (HF level with small basis sets) and considered only the C=C addition, the catalytic effect brought about by the actively involved second water molecule has been clearly pointed out. Here again, geometrical parameters of the actively participating water molecules are included as a basic part of the reaction coordinates. Fig. 1, 2 and 3 show transition structures (TS) and products for the additions with respectively one, two and three water molecules. While Tables 1 and 2 collect total, relative and zero-point energies of all gas-phase structures calculated, Table 3 lists the energies in aqueous solution computed using the PCM model. In Table 4, energy barriers obtained for reactions with different chains of water molecules are reported.

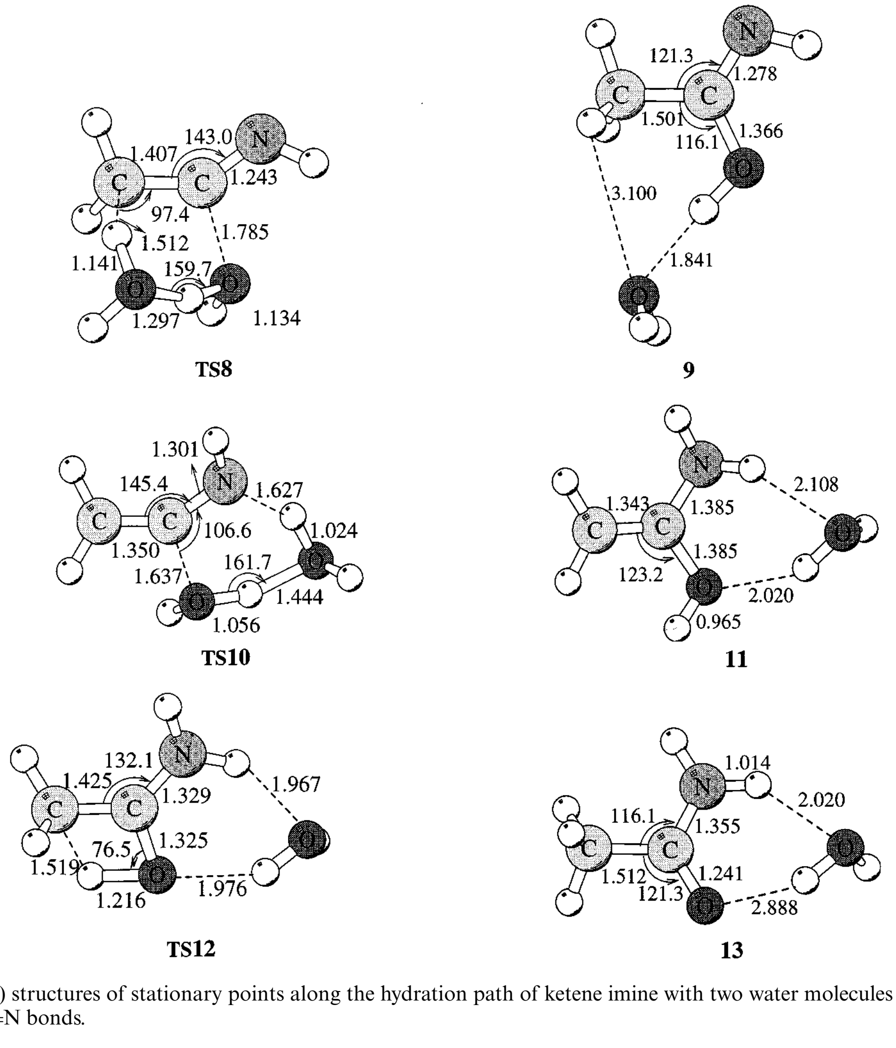
For both C=N and C=C additions, only cyclic TS's have been found, involving a concerted action of the nucleophilic attack of the oxygen and the hydrogen transfer to a terminal atom. Attempts to locate a more open TS in which the hydrogen atom of the water cluster lies far away from the terminal centre were not successful, even in the solvent continuum. Similarly, no zwitterionic intermediates could be located either in the gas phase or in aqueous solution.

The results obtained with different methods are internally consistent showing clearly that for the one- and two-water cases, addition of water across the C=N bond is favoured over the one across the C=C bond of ketene imine. Without any help from assisting water molecules (one-water system), the hydration barrier across the C=N bond is found to be about 11 kJ mol^{-1} lower than the corresponding one across C=C. Moreover, it can be observed that upon an increase of the number of water molecules which make up the chain, the energy barrier diminishes for both types of addition. As expected, inclusion of a

Table 1 Calculated total energies (hartree) and zero-point vibrational (ZPE, kJ mol^{-1}) energies for structures related to the hydration of ketene imine

Absolute energies	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)	ZPE[c]
$H_2C{=}C{=}NH$ **1**	−131.87953	−132.31787	−132.35792	−132.34591	−132.34527	101
H_2O	−76.02361	−76.21979	−76.27491	−76.23165	−76.23158	55
$H_2C{=}C{=}NH + H_2O$	−207.90314	−208.53766	−208.63283	−208.57756	−208.57685	156
TSCC **TS2**	−207.80455	−208.45489	−208.55890	−208.50348	−208.50211	154
$H_3C–C–NH–OH$ **3**	−207.96363	−208.58837	−208.68635	−208.63991	−208.63926	181
TSCN **TS4**	−207.81823	−208.46209	−208.56751	−208.51104	−208.51015	164
$H_2C{=}C–NH_2–OH$ **5**	−207.94420	−208.56520	−208.66820	−208.61643	−208.61591	180
TS 1,3-H-shift **TS6**	−207.85940	−208.49819	−208.60122	−208.54629	−208.54539	167
$H_3C–CONH_2$ **7**	−207.98897	−208.61178	−208.70928	−208.66147	−208.66065	185
$H_2C{=}C{=}NH + 2\,H_2O$	−283.92675	−284.75745	−284.90774	−284.80921	−284.80843	211
TSCC **TS8**	−283.85220	−284.70988	−284.86321	−284.76801	−284.76669	226
$H_3C–C–NH–OH \cdots H_2O$ **9**	−283.99779	−284.82169	−284.96804	−284.88474	−284.88002	249
TSCN **TS10**	−283.87876	−284.72410	−284.87951	−284.78356	−284.78258	237
$H_2C{=}C–NH_2–OH \cdots H_2O$ **11**	−283.97761	−284.79975	−284.95347	−284.86234	−284.86170	250
TS 1,3-H-shift **TS12**	−283.89796	−284.73837	−284.89113	−284.79785	−284.79684	238
$H_3C–CONH_2 \cdots H_2O$ **13**	−284.02817	−284.85234	−284.99888	−284.91337	−284.91243	251
$H_2C{=}C{=}NH + 3\,H_2O$	−359.95036	−360.97724	−361.18265	−361.04086	−361.04001	266
TSCC **TS14**	−359.91644	−360.96839	−361.17466	−361.03716	−361.03611	304
$H_3C–C–NH–OH \cdots 2H_2O$ **15**	−360.03546	−361.05972	−361.26285	−361.13384	−361.13300	314
TSCN **TS16**	−359.90839	−360.96391	−361.17117	−361.03295	−361.03188	302
$H_2C{=}C–NH_2–OH \cdots 2H_2O$ **17**	−360.01442	−361.03727	−361.24244	−361.11090	−361.11015	314
TS 1,3-H-shift **TS18**	−359.93851	−360.97996	−361.18441	−361.05038	−361.04927	303
$H_3C–CONH_2 \cdots 2H_2O$ **19**	−360.06900	−361.09398	−361.29231	−361.16601	−361.16497	316

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries. [c] Zero-point energies from HF/6-31G(d,p) and scaled by 0.9.



TS8 **9**

TS10 **11**

TS12 **13**

Fig. 2 MP2/6-31G(d,p) structures of stationary points along the hydration path of ketene imine with two water molecules ($H_2C{=}C{=}NH + 2\,H_2O$) across both C=C and C=N bonds.

second water in the supermolecule tends to decrease substantially the energy barrier of C=C addition by 69 kJ mol^{-1} and that of C=N addition by 89 kJ mol^{-1}. This gives rise to an overall preference of 31 kJ mol^{-1} in favor of the C=N addition over the C=C. Due to the distortion around the terminal CH_2 group of ketene imine during the transition state of water

Table 2 Calculated relative energies (kJ mol^{-1}) for the various hydrations of ketene imine, all corrected by zero-point vibrational energies (ZPE, kJ mol^{-1})

Relative energies	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)
$H_2C=C=NH + H_2O$	0	0	0	0	0
TSCC **TS2**	257	215	192	192	194
$H_3C–C–NH–OH$ **3**	−184	−108	−116	−139	−139
TSCN **TS4**	231	206	179	183	183
$H_2C=C–NH_2–OH$ **5**	−84	−48	−69	−78	−79
TS 1,3-H-shift **TS6**	126	115	94	93	94
$H_3C–CONH_2$ **7**	−196	−166	−172	−191	−191
$H_2C=C=NH + 2\,H_2O$	0	0	0	0	0
TSCC **TS8**	211	147	132	123	125
$H_3C–C–NH–OH \cdots H_2O$ **9**	−149	−124	−120	−160	−150
TSCN **TS10**	152	121	100	93	94
$H_2C=C–NH_2–OH \cdots H_2O$ **11**	−95	−65	−81	−100	−101
TS 1,3-H-shift **TS12**	103	84	71	57	57
$H_3C–CONH_2 \cdots H_2O$ **13**	−226	−202	−199	−233	−233
$H_2C=C=NH + 3\,H_2O$	0	0	0	0	0
TSCC **TS14**	127	61	59	48	48
$H_3C–C–NH–OH \cdots 2H_2O$ **15**	−175	−155	−163	−196	−196
TSCN **TS16**	146	85	66	57	57
$H_2C=C–NH_2–OH \cdots 2H_2O$ **17**	−120	−96	−109	−136	−136
TS 1,3-H-shift **TS18**	68	44	32	12	13
$H_3C–CONH_2 \cdots 2H_2O$ **19**	−261	−243	−238	−279	−278

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries.

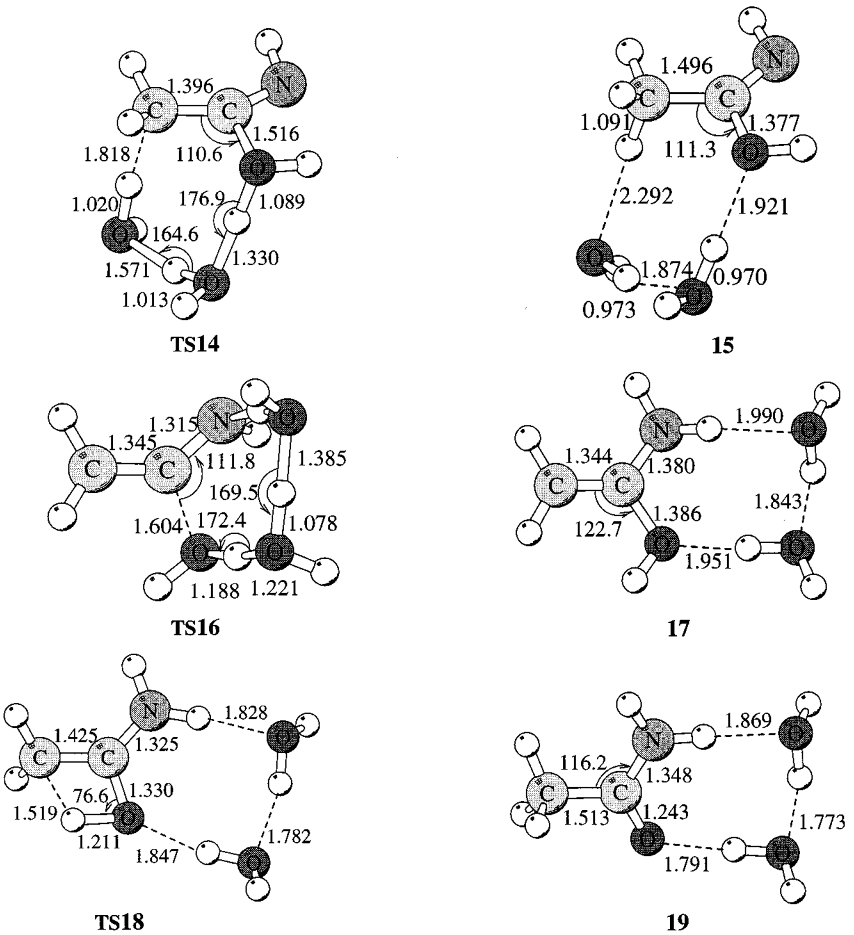


Fig. 3 MP2/6-31G(d,p) structures of stationary points along the hydration path of ketene imine with three water molecules ($H_2C=C=NH + 3\,H_2O$) across both C=C and C=N bonds.

addition across the C=C bond, the corresponding energy barrier is relatively higher than that for addition across the C=N bond, where little distortion is induced by attack of water.

The most interesting result of the present study is perhaps the fact that a reverse situation occurs when a chain of three water molecules is taken into effect. Now there is a proclivity to perform the C=C addition in a slightly easier way than the C=N addition, the former TS lying about 9 kJ mol^{-1} lower in energy than the latter. Although such an energy difference is rather small in view of the accuracy of the computed values, estimated to be ±12 kJ mol^{-1}, the reversal of energy order strongly indicates a trend and this finding is consistent with experimental evidence for direct formation of C=C products, without primary formation of amide enols, in phenyl- and diphenylketene imines.[3] An energy barrier of 48 kJ mol^{-1} is calculated at the CCSD(T)/6-31G(d,p) level of theory, the lowest barrier of all the examined water chain models.

Fig. 4 displays schematic energy profiles showing the calculated activation energies for hydration of ketene imine including water chains going from one to three ($H_2C{=}C{=}NH + n\ H_2O \rightarrow H_2CONH_2 + (n-1)\ H_2O$, $n = 1, 2, 3$). All energy barriers are shown relative to the separated species. From Fig. 4, the different behaviour of the three-water case can be emphasized. While, in the latter, the energy barrier for C=N addition is the highest among both possible additions, the one- and two-water cases give rise to a lowering of respectively 11 and 31 kJ mol^{-1}, in favour of the C=N addition. These findings can be understood in looking at the geometric parameters displayed in Fig. 1–3. While attack on ketene imine by one- and two-water chains essentially occurs in one plane, addition by a cluster of three water molecules tends to happen in two quasi perpendicular planes. This results, in the three-water case, in smaller ring strain and more importantly, less inconvenience for C=C addition by causing a smaller distortion of the CH_2 group around the double bond. Therefore, the latter is markedly accelerated. In transition structure **TS14** across the C=C bond on one end, hydrogen attacks at the β-carbon of ketene imine in a plane containing the π orbitals of the C=C bond; on the other end of the cluster, oxygen attacks at the α-carbon in a plane perpendicular to the former. The ketene imine can thus vibrate following its normal mode of bending and/or distortion. Similarly, in **TS16** across the C=N bond, a chain of three water molecules attacks in two different planes. The reactivity of ketene imine is no longer dominated by the energy required for methylene distortion, but now enjoys a significant back donation of electron pair density from the formal nitrogen lone pair to the β-carbon. This is particularly significant due to the short α-carbon–nitrogen bond and the spatial position of the orbitals involved. A “carbanion” character of the β-carbon

Table 3 Total (hartree) and relative (kJ mol^{-1}) energies of the considered stationary points along the ketene imine hydration path including a solvent continuum ($\varepsilon = 78.3$), using the PCM method. All relative values are corrected by zero-point energies

	Total energies[a]	Relative energies[a]
$H_2C{=}C{=}NH$	−132.30860	—
H_2O	−76.23049	—
$H_2C{=}C{=}NH + H_2O$	−208.53909	0
TSCC **TS2**	−208.46445	194
H_3C–C–NH–OH **3**	−208.60079	−137
TSCN **TS4**	−208.47137	186
$H_2C{=}C$–NH_2–OH **5**	−208.57571	−72
TS 1,3-H-shift **TS6**	−208.50656	96
H_3C–$CONH_2$ **7**	−208.62582	−199
$H_2C{=}C{=}NH + 2\ H_2O$	−284.76958	0
TSCC **TS8**	−284.72579	130
H_3C–C–NH–OH···H_2O **9**	−284.84282	−154
TSCN **TS10**	−284.73655	113
$H_2C{=}C$–NH_2–OH···H_2O **11**	−284.81597	−83
TS 1,3-H-shift **TS12**	−284.75041	77
H_3C–$CONH_2$···H_2O **13**	−284.87244	−230
$H_2C{=}C{=}NH + 3\ H_2O$	−361.00007	0
TSCC **TS14**	−360.99355	55
H_3C–C–NH–OH···$2H_2O$ **15**	−361.08634	−179
TSCN **TS16**	−360.98786	68
$H_2C{=}C$–NH_2–OH2···H_2O **17**	−361.05965	−108
TS 1,3-H-shift **TS18**	−360.99706	45
H_3C–$CONH_2$···$2H_2O$ **19**	−361.11695	−257

[a] Results from PCM-MP2/6-31G(d,p) calculations for a continuum having relative permittivity $\varepsilon = 78.3$, and based on gas-phase optimized geometries at the MP2/6-31G(d,p) level.

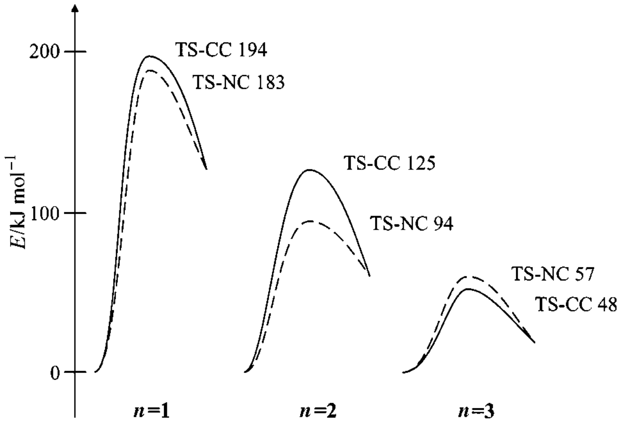


Fig. 4 Schematic energy profiles showing the activation energies for hydration of ketene imine including different numbers of water molecules ($H_2C{=}C{=}NH + n\ H_2O$), calculated at the CCSD(T)/6-31G(d,p)// MP2/6-31G(d,p) + ZPE level of theory. All energy barriers are relative to the separated species.

Table 4 Energy barriers (kJ mol^{-1}) for the hydration of ketene imine, including different water clusters ($H_2C{=}C{=}NH + n\ H_2O \rightarrow H_3C$–$CONH_2 + (n-1)\ H_2O$, $n = 1, 2, 3$), both in the gas phase and in aqueous solution

	Gas phase					Solution
	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)	PCM-MP2[c] 6-31G(d,p)
1 H_2O						
CC	257	215	192	192	194	194
CN	231	206	179	183	183	186
2 H_2O						
CC	211	147	132	123	125	130
CN	152	121	100	93	94	113
3 H_2O						
CC	127	61	59	48	48	55
CN	146	85	66	57	57	68
1,3-H-shift 1	210	163	163	171	173	168
1,3-H-shift 2	198	149	152	157	158	160
1,3-H-shift 3	188	140	141	148	149	153

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries. [c] Results from PCM-MP2/6-31G(d,p) calculations, based on gas phase geometries at the MP2/6-31G(d,p) level.

Table 5 Calculated total energies (hartree) and zero-point vibrational (ZPE, kJ mol^{-1}) energies for the hydration of carbodiimide

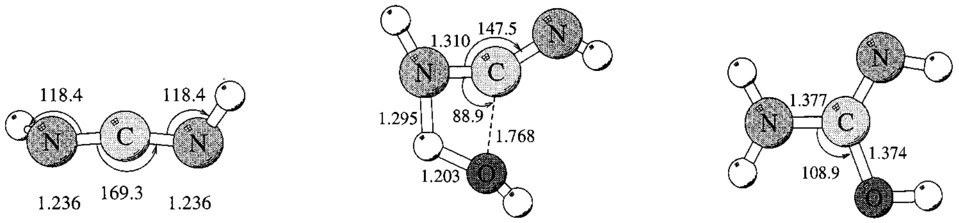
Absolute energies	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)	ZPE[c]
HN=C=NH **1**	−147.90395	−148.35833	−148.42214	−148.39048	−148.38942	83
H_2O	−76.02361	−76.21979	−76.27491	−76.23165	−76.23158	55
HN=C=NH **1** + H_2O	−223.92756	−224.57812	−224.69705	−224.62213	−224.62100	−138
TS **TS21**	−223.84397	−224.51972	−224.63280	−224.56054	−224.55922	−143
H_2N–C–NH–OH **3**	−223.96847	−224.61479	−224.72740	−244.65906	−224.65837	−162
HN=C=NH **1** + $2H_2O$	−299.95117	−300.79791	−300.97196	−300.85378	−300.85258	−193
TS **TS23**	−299.90417	−300.77978	−300.94329	−300.83119	−300.82995	−210
H_2N–C–NH–OH ··· H_2O **5**	−300.00140	−300.84878	−301.01212	−300.90441	−300.90360	−224
HN=C=NH **1** + $3H_2O$	−375.97478	−377.01770	−377.24687	−377.08543	−377.08316	−248
TS **TS25**	−375.94416	−377.02167	−377.23714	−377.08359	−377.08244	−281
H_2N–C–NH–OH ··· $2H_2O$ **7**	−376.03986	−377.08769	−377.30358	−377.15465	−377.15374	−287

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries. [c] Zero-point energies from HF/6-31G(d,p) and scaled by 0.9.

Table 6 Calculated relative energies (kJ mol^{-1}) for the hydration of carbodiimide, all corrected for zero-point vibrational energies (ZPE)

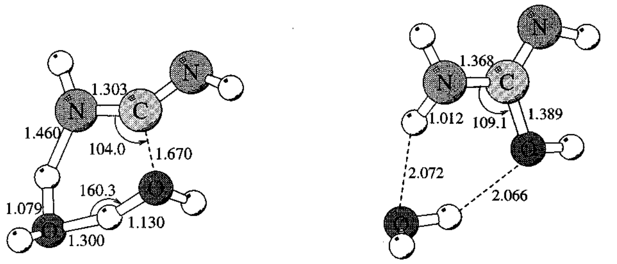
Relative energies	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)
HN=C=NH **1** + H_2O	0	0	0	0	0
TS **TS21**	224	158	174	166	167
H_2N–C–NH–OH **3**	−83	−72	−56	−73	−74
HN=C=NH **1** + $2H_2O$	0	0	0	0	0
TS **TS23**	140	65	92	76	76
H_2N–C–NH–OH ··· H_2O **5**	−101	−103	−73	−102	−103
HN=C=NH **1** + $3H_2O$	0	0	0	0	0
TS **TS25**	113	23	59	38	38
H_2N–C–NH–OH ··· $2H_2O$ **7**	−132	−145	−110	−143	−144

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries..



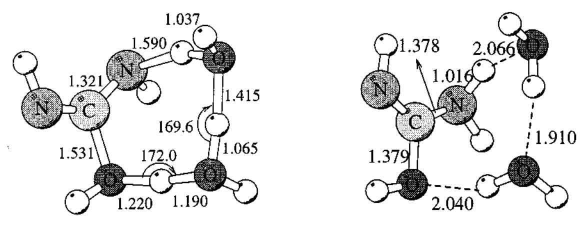
20 **TS21** **22**

Fig. 5 MP2/6-31G(d,p) structures of stationary points along the hydration path of carbodiimide with one water molecule (HN=C=NH + H_2O).



TS23 **24**

Fig. 6 MP2/6-31G(d,p) structures of stationary points along the hydration path of carbodiimide with two water molecules (HN=C=NH + 2 H_2O).



TS25 **26**

Fig. 7 MP2/6-31G(d,p) structures of stationary points along the hydration path of carbodiimide with three water molecules (HN=C=NH + 3 H_2O).

is well reflected in the reaction of ketene imines with electrophiles at this β-carbon, and the lower basicity of the nitrogen.[3–5] Calculations for the 1,3-H-transfer from the primary product, following the C=N addition, give energy barriers of 173 (from **5** to **TS16**), 158 (from **11** to **TS12**) and 149 (from **17** to **TS18**) kJ mol^{-1}, respectively without and with one and two interacting (but not participating) water molecules. It seems that extension to another passively interacting water molecule leads to an electrostatic stabilization of only about 10 kJ mol^{-1}. An active water molecule has thus to be included in order to assist the 1,3-H-shift. Similarly, the assisting water molecule tends to lower the energy needed to perform the hydrogen shift dramatically, resulting now in an energy barrier of only 59 kJ mol^{-1} for the 1,3-H-shift connecting both isomeric adducts. Note that the corresponding energy barrier of 59 kJ mol^{-1} is negligible when compared with the barrier for C=N addition of water, the preceding step in the reaction path. Therefore, the 1,3-H-shift is not rate limiting and can be ignored when searching for the energetically most favoured reaction path. Overall, the present results suggest that water oligomers higher than the dimer seem to make an appreciable, if not essential, contribution to the reaction rate and are likely to be involved in a concerted hydration of ketene imines.

Hydration of carbodiimide (HN=C=NH)

Relatively little is known about the hydration process of carbodiimide.[15,16] It appears that ureas have been observed as final products. The structure and properties of the parent carbodiimide (HN=C=NH) have been studied by different methods.[17–19] Figs. 5 to 7 show the optimized structures of the initial complexes and the TS's along the hydration reaction path of carbodiimides including a chain of one, two and three water molecules. The corresponding total, relative and zero-point energies are given in Tables 5 and 6. Energy barriers for the different reaction pathways are reported in Table 7. In the case of unsubstituted carbodiimide, addition of water is only possible across one C=N bond. Compared with the addition of water across the C=N bond of ketene imine, a decrease of about 20 kJ mol^{-1} could be observed in going from ketene imine to carbodiimide, no matter how many water molecules are involved in the reaction path. This fact can be understood by the presence of two nitrogen centres in carbodiimide which makes the molecule more polarized and the central carbon atom more "electrophilic". This results in an easier two-site attack of the water system even though the TS is somewhat later in carbodiimide than in ketene imine. The resulting new C–O bond has in fact been more developed at **TS25** of carbodiimide (the C–O length being 1.531 Å, Fig. 7) than at **TS16** of ketene imine (1.604 Å, Fig. 5). A seemingly determining factor for the difference in energy barrier is the inherent configurational instability of carbodiimide.[17,18] It is well established that the inversion and/or distortion of this cumulene is a rather facile process; in any case it is much more facile than the structural distortion in the more rigid ketene imine. Overall, in the hydration of carbodiimides a chain of at least three water molecules is apparently necessary in order to efficiently transfer the proton from the oxygen to the nitrogen.

The effect of bulk solvent

The next step in our investigation was to study the bulk solvent effect on the energetic features of the reaction paths and to compare these values with those observed for the gas phase. The total and relative energies calculated in a solvent continuum are summarized in Tables 3 and 4 for the hydration of ketene imine and in Tables 7 and 8 for that of carbodiimide. Inspection of the data for ketene imine indicates that the electrostatic solvation energies computed using the PCM model tend to decrease the activation energies relative to those obtained in the gas phase at the same level. Nevertheless, as activation energies for one, two and three water molecules change by the same amount, the relative order for preferential attack across C=C or C=N bonds is not modified. Therefore, the conclusions drawn from gas-phase calculations are still valid. Concerning the carbodiimide reaction, the solvent continuum seems to increase the activation energies by a significant amount as compared with gas-phase results at the same level of theory. The reason for such an increase is not clear to us. However, the PCM results do not modify the overall gas-phase findings, as was the case for ketene imine. It is clear that the hydration of both ketene imine and carbodiimide in aqueous solution is another case of an active solvent effect which is the key factor in the reaction.[20–23]

Table 7 Total (hartree) and relative (kJ mol^{-1}) energies of the considered stationary points for the hydration of carbodiimide including a solvent continuum ($\varepsilon = 78.3$), using the PCM method. All relative values are corrected by ZPE's

	Total energies[a]	Relative energies
HN=C=NH **1**	−148.36688	—
H_2O	−76.23051	—
HN=C=NH **1** + H_2O	−224.59739	0
TS **TS21**	−224.53225	176
H_2N–C–NH–OH **3**	−224.63244	−68
HN=C=NH **1** + $2H_2O$	−300.82790	0
TS **TS23**	−300.80059	89
H_2N–C–NH–OH $\cdots$ H_2O **5**	−300.87311	−88
HN=C=NH **1** + $3H_2O$	−377.05841	0
TS **TS25**	−377.05504	42
H_2N–C–NH–OH $\cdots$ $2H_2O$ **7**	−377.11877	−119

[a] Based on MP2/6-31G(d,p) gas-phase geometries.

Concluding remarks

In the present paper, a theoretical study of the hydration mechanism of ketene imine and carbodiimide has been undertaken. It is shown that specific interaction of water chains represents an efficient way to achieve the hydration of ketene imines. This can occur in the hydration reaction with excess water or in aqueous solution. In the latter case, it thus constitutes an active solvent effect. Using one and two actively participating water molecules to model the hydration reaction, calculated results consistently show that the addition of water across the C=N bond, giving first an amide enol, is favoured over C=C addition, yielding immediately the amide product. A reverse situation occurs when a chain of three water molecules is used to model the process, where attack of a water cluster in two distinct planes is now possible, and the C=C addition becomes easier to perform than the C=N. These findings are in accordance with experimental evidence for direct formation of C=C products in non-hindered materials. An energy barrier of 48 kJ mol^{-1} is found at the CCSD(T)/6-31G(d,p) level of theory, the lowest barrier of all water chain models considered. It is apparent that oligomers higher than the dimer of water are needed to allow a rapid concerted reaction. The hydration of carbodiimide, another member of the cumulene family, which occurs at the C=N bond, is invariably more facile than that of ketene imine.

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Table 8 Activation energies (kJ mol^{-1}) for the hydration of carbodiimide, including different numbers of solvent molecules (HN=C=NH + n $H_2O \rightarrow H_2N$–$CONH_2$ + $(n - 1)$ H_2O, $n = 1, 2, 3$), both in the gas phase and in solution

	Gas phase					Solution
	HF[a] 6-31G(d,p)	MP2[b] 6-31G(d,p)	MP2[b] 6-311++G(d,p)	QCISD(T)[b] 6-31G(d,p)	CCSD(T)[b] 6-31G(d,p)	PCM-MP2[c] 6-31G(d,p)
1 H_2O	224	158	174	166	167	176
2 H_2O	140	65	92	76	76	89
3 H_2O	113	23	59	38	38	42

[a] Based on HF/6-31G(d,p) geometries. [b] Based on MP2/6-31G(d,p) geometries. [c] Results from PCM-MP2/6-31G(d,p) calculations, based on gas-phase geometries at the MP2/6-31G(d,p) level.

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