Mechanism of the Beckmann rearrangement in sulfuric acid solution

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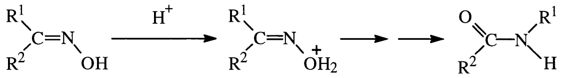
***Ab initio* calculations have been performed to probe the mechanism of the Beckmann rearrangement of formaldehyde oxime in concentrated sulfuric acid or in oleum solution ($H_2SO_4 + S_2O_7$). In the gas phase, the most favoured reaction path is: protonation of oxime ⟶ N-protonated oxime ⟶ O-protonated oxime ⟶ fragmentation products, in which the 1,2-H-shift connecting both protonated forms constitutes the rate-determining step. Reaction field calculations using two different models [Onsager self-consistent reaction field (SCRF) and polarizable continuum model (PCM)] indicate that the non-specific interaction of the solvent exerts only a small effect on both the energetic and geometrical parameters of the considered reaction path. Formation of the sulfate ester, $H_2C{=}N{-}O{-}SO_3H$, also appears to play a negligible role in marginally affecting the 1,2-H-shift. In contrast, a specific interaction between solvent molecules and substrates seems to be the dominant factor in reducing substantially the energy barrier to 1,2-H-shift. Using a neutral H_2SO_4 molecule as a simple model for solvent molecules, MP2/6-311G(d,p) energy calculations based on HF/6-31G(d)-geometries of the supermolecule reveal that the barrier to 1,2-H-shift is decreased by 115 kJ mol^{-1} with respect to the gas phase value, when a H_2SO_4 molecule interacts specifically with the protonated oxime and thereby assists the hydrogen migration. The calculated results thus suggest a strong case of active solvent participation in which the solvent molecules exert a catalytic effect.**

Introduction

The Beckmann rearrangement (designated hereafter as BR), in which an oxime is converted into its more stable amide isomer, was first described more than a century ago.[1] Since then, this transformation has been employed in a variety of ways in organic syntheses.[2,3] One of the most popular applications of the BR is the conversion of cyclohexanone oxime into ε-caprolactam; the latter turns out to be an important industrial chemical which yields Nylon-6 after polymerization. In spite of the large number of experimental studies devoted to the BR, its detailed mechanism remains poorly understood.

The BR is mainly an acid–base process in which the initial step involves a protonation of the oxime. Although different acidic solutions have been used experimentally for this purpose, two of them have emerged as the most efficient treatments, namely, a Beckmann mixture and an oleum solution.[4] While a Beckmann mixture consists of a solution of acetic acid and acetic anhydride, saturated with gaseous hydrogen chloride, an oleum solution contains sulfuric acid and sulfur trioxide ($H_2SO_4 + SO_3$). An aqueous solution of concentrated sulfuric acid, with more than 85–90% H_2SO_4, can also be used. In more dilute aqueous solutions of H_2SO_4, alicyclic oximes undergo hydrolysis rather than BR. In the industrial manufactue of ε-caprolactam, a concentrated sulfuric acid solution or an oleum solution is also used as the solvent during the entire acidic step until the primary products are treated by a basic solution.[4] Concerning the BR mechanism, it has commonly been assumed that the protonation occurs at the oxygen atom of the oxime followed by a migration from carbon to nitrogen of a substituent situated in an anti position to the departing hydroxy group [reaction (1)].



(1)

In recent theoretical studies on model systems,[5–7] we have, however, pointed out the inconsistencies in the current conventional wisdom and now set out to tackle three fundamental questions about the BR mechanism, namely (i) the identity of the rate-determining step; (ii) the influence of the substituents and (iii) the effect of the solvent used. In earlier papers[5–7] devoted to the first question, we have shown that the energetically most favoured route in the gas phase is as follows: protonation of oxime ⟶ N-protonated oxime ⟶ O-protonated oxime ⟶ fragmentation products. Since protonation occurs without any barrier, all the protonated species are expected to be formed. Nevertheless, due to the large energy difference between both N- and O-protonated oximes amounting to more than 70 kJ mol^{-1}, the N-protonated form should be largely preferred upon protonation. The O-protonated species does exist but its population is expected to be quite small. The equilibrium should be strongly, if not completely, displaced towards the N-isomer. Because the less stable O-protonated form has the appropriate nuclear configuration for a migration–elimination, it is reasonable to admit that its formation from the N-protonated form turns out to be a necessary step of the BR. This conversion through a simple 1,2-hydrogen shift constitutes the rate-determining step with an energy barrier of about 220 kJ mol^{-1} in protonated formaldehyde oxime. Transformation of the O-protonated form which involves a migration from C to N and is in concert with a water departure, is classically called a BR and has been shown to be a more facile process,[6–7] the associated energy barrier being less than about 40 kJ mol^{-1}. Thus, the most significant result is that our calculated energy barrier for the rate-controlling 1,2-H migration step is far larger than the experimental values of about 100 kJ mol^{-1} for several substituted oximes using different solvents.[4,8,9] Such an inconsistency suggests an important effect of the substituents and/or the solvent employed. We have recently worked out the influence of methyl substitution at carbon and substitution at oxygen by methyl and formyl groups.[7b] It appears that in *C*-dimethyl oxime, the barrier for the migration–elimination step is reduced to about 10 kJ mol^{-1}. On the other hand, our results indicate that the energy barrier of the rate-determining 1,2-H-shift is not modified significantly when substituent effects are taken into account. Hence, the solvent is expected to play a

Table 1 Calculated total, zero-point and relative energies of the considered stationary points, with and without sulfate substituent

Total energies				
Structure[a,b]	HF 6-31G(d)	HF 6-31G(d,p)	MP2 6-311G(d,p)	ZPE[c]
$H_2C=NH-OH(+)$ **N**	−169.169 93	−169.224 34	−169.728 26	149
1,2-H-shift **TS1**	−169.046 63	−169.105 02	−169.634 42	130
$H_2C=N-OH_2(+)$ **O**	−169.130 84	−169.186 93	−169.695 26	143
Rearrangement **TS2**	−169.097 66	−169.161 01	−169.666 95	121
$HC=NH\cdots H_2O(+)$ **C**	−169.213 86	−169.278 05	−169.794 35	131
$HC=NH(+) + H_2O$ **F**	−169.169 79	−169.232 90	−169.741 36	126
$H_2C=NH-OSO_3H(+)$ **Ns**	−791.171 35	−791.294 95	−792.531 57	189
1,2-H-shift **TS1s**	−791.044 49	−791.172 90	−792.439 60	168
$H_2C=N-OH-SO_3H(+)$ **Os**	−791.121 65	−791.248 33	−792.497 52	181
Rearrangement **TS2s**	−791.118 77	−791.247 07	−792.477 50	174
$HC=NH\cdots H_2SO_4(+)$ **Cs**	−791.218 70	−791.352 91	−792.590 16	175
$HC=NH(+) + H_2SO_4$ **Fs**	−791.197 96	−791.332 70	−792.562 97	173

Relative energies[d]	HF 6-31G(d)	HF 6-311G(d,p)	MP2 6-311G(d,p)
$H_2C=NH-OH(+)$ **N**	−97	−92	−81
1,2-H-shift **TS1**	207	202	147
$H_2C=N-OH_2(+)$ **O**	0	0	0
Rearrangement **TS2**	65	46	52
$HC=NH\cdots H_2O(+)$ **C**	−229	−251	−272
$HC=NH(+) + H_2O$ **F**	−119	−138	−138
$H_2C=NH-OSO_3H(+)$ **Ns**	−122	−114	−81
1,2-H-shift **TS1s**	193	−185	139
$H_2C=N-OH-SO_3H(+)$ **Os**	− 0	0	0
Rearrangement **TS2s**	1	−4	46
$HC=NH\cdots H_2SO_4(+)$ **Cs**	−261	−281	−249
$HC=NH(+) + H_2SO_4$ **Fs**	−208	−230	−179

[a] The letter **s** stands for sulfate derivatives. [b] Based on HF/6-31G(d) geometries. [c] Based on HF/6-31G(d) vibrational wavenumbers and scaled by 0.9. [d] Including ZPE corrections.

crucial role. In the present work, we attempt to probe solvent effects by carrying out calculations on model systems. For this purpose, long range non-specific interactions are examined using both the Onsager SCRF and PCM continuum methods, as well as the specific interaction using the supermolecule technique in which a neutral sulfuric acid molecule interacts and modifies the energy profile of the reaction path. The possibility of changes in geometrical reaction coordinates in the presence of the solvent is also studied, as well as a preliminary formation of the sulfate esters ($H_2C=N-O-SO_3-H$).

Calculations

Ab initio molecular orbital (MO) calculations were carried out with the aid of the GAUSSIAN 94 set of programs.[9] The stationary points of each system considered were initially located and characterized by harmonic vibrational analyses at the Hartree–Fock level (HF)[10] with the 6-31G(d) basis set. When possible, geometrical parameters of the relevant equilibrium and transition structures have been reoptimized using second-order perturbation theory (MP2)[11] with the same one-electron functions. Improved relative energies between the stationary points were subsequently estimated using the larger 6-311G(d,p) basis set and corrected for zero-point vibrational energies (ZPE). Concerning the non-specific interaction of the solvent, we have adopted two different reaction field models: the Onsager self-consistent reaction field (SCRF) algorithm implemented by Wiberg and co-workers,[12] as well as the more evolved polarizable continuum model (PCM) developed by Tomasi and co-workers.[13] While the former only considers spherical cavities, the latter considers a cavity whose shape is well adapted to the molecular geometry in such a way that the solute–solvent interactions could be better described. To study the specific interaction between solute and solvent, MO calculations using the supermolecule approach were performed including one or more solvent molecules in the reaction coordinate. Throughout this paper, bond lengths are given in Å, bond angles in degrees, total energies in hartrees and zero-point and relative energies in kJ mol^{-1}.

Results and discussion

Gas phase reaction

We have recently reported calculations related to the mechanism of the Beckmann rearrangement in the gas phase.[7] It may be useful to recall the essential results. A predominant N-protonation of formaldehyde oxime gives rise to a N-protonated form which should in turn be converted to its less stable O-protonated isomer through a 1,2-shift of the hydrogen. This step is followed by a migration–elimination, which has a much lower energy barrier. Relative energies between points on the reaction pathway obtained by MP4SDTQ, QCISD and QCSID(T) calculations with basis sets up to 6-311++G(2df,2p) are rather similar, the differences lying within the expected error bars. This indicates that energies of the structures under consideration can reasonably be estimated by using MP2 expansions, which are chosen for the present study. For the sake of consistency, the reaction path of the unsubstituted system [CH_4NO^+] has been recalculated at the MP2/6-311G(d,p) level using HF/6-31G(d) optimized geometries. The total and relative energies are summarized in Table 1. Thus, the 1,2-H-shift connecting the N- to the O-protonated oxime is identified as the key step in a gas phase BR.

Reaction in solvent

Let us first mention the electrostatic influence of the solvent. As

Table 2 Calculated total[a] and relative energies (in parentheses) of the considered stationary points, both in gas phase ($\varepsilon = 1$) and solvent ($\varepsilon = 78.3$), using two different continuum models

		Including reaction field energy	
	Without reaction field	SCRF[b]	PCM[c]
$H_2C{=}NH{=}OH(+)$ **N**	−169.169 93 (0)	−169.175 07 (0)	−169.303 62 (0)
1,2-H-shift **TS1**	−169.046 63 (324)	−169.048 04 (334)	−169.174 41 (339)
$H_2C{=}N{-}OH_2(+)$ **O**	−169.130 84 (103)	−169.132 78 (111)	−169.258 95 (117)
Rearrangement **TS2**	−169.097 66 (190)	−169.106 02 (181)	−169.227 69 (199)
$H_2C{=}NH{-}OH \cdots H_2SO_4$ complex (+) **NS**	−867.242 70 (0)	−867.252 29 (0)	867.36822 (0)
TS 1,2-H-shift **TS1S**	−867.184 49 (153)	−867.190 28 (163)	−867.307 14 (160)
$H_2C{=}NH{-}OH_2 \cdots H_2SO_4$ complex (+) **OS**	−867.206 53 (95)	−867.212 00 (106)	−867.328 01 (106)

[a] All results are based on gas phase HF/6-31G(d) optimized geometries. [b] Onsager self-consistent reaction field (SCRF) model, as implemented in Gaussian 94.[9] [c] Polarizable continuum model (PCM) developed by Tomasi and co-workers and implemented in Gaussian 94.

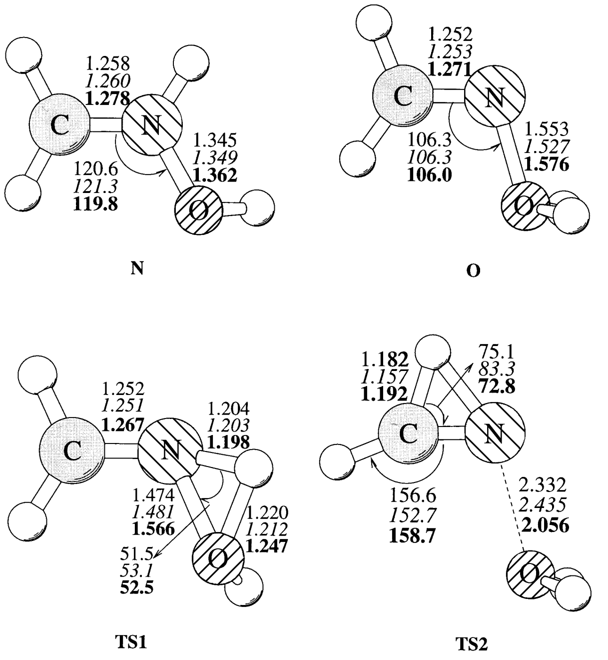


Fig. 1 Main geometrical features of the critical points along the Beckmann reaction path, both in the gas phase and in the solvent. Different letter styles (italic, bold) are used to distinguish calculations in the gas phase ($\varepsilon = 1$) and in the solvent ($\varepsilon = 78.3$), at different levels: HF/6-31G(d) geometries in the gas phase; *HF/6-31G(d) geometries in the solvent*; **MP2/6-31G(d,p) geometries in the gas phase**.

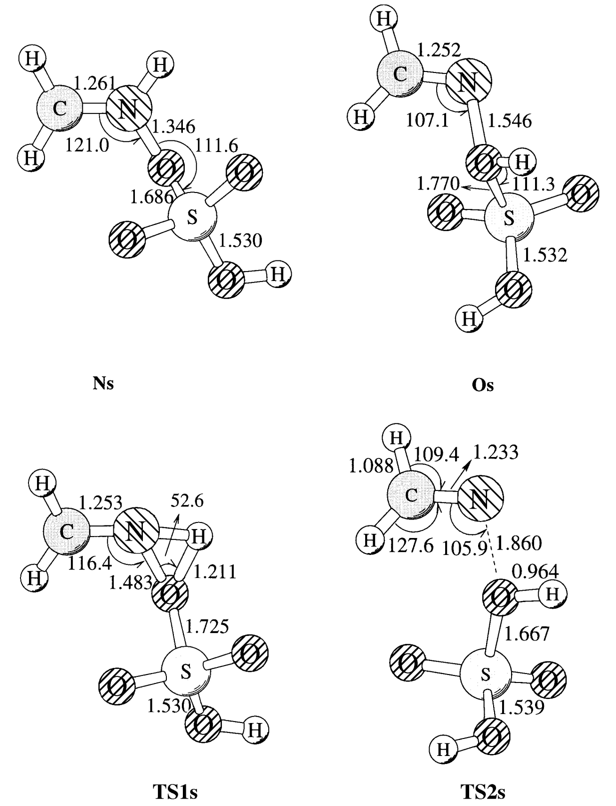


Fig. 2 Selected HF/6-31G(d) geometrical parameters of structures related to the transformation of protonated sulfate esters. The letter **s** stands for a sulfate group.

shown in Table 2, solvation energies in water solvent ($\varepsilon = 78.3$), calculated by either the Onsager SCRF model or the PCM method, cause only a small modification of the gas phase reaction path. Results from a continuum treatment on geometrical structures of the supermolecules are also recorded in Table 2. For both 1,2-H-shift and migration–elimination steps, a change in energy barrier of at most 10 kJ mol^{-1} can be noted upon incorporation of the solvent reaction field. In order to probe further the effect of the continuum on geometrical parameters, the critical points were optimized in solvent taking gas phase structures as starting points and using the Onsager SCRF method. Selected geometrical parameters in gas phase and in solvent of both N- and O-protonated species, as well as the relevant transition structures, are shown in Fig. 1. From these optimized structures, there is no doubt that long range solvent interactions exert no significant influence on the gas phase reaction coordinates; the main characteristics of the gas phase BR remain valid in solution. It seems therefore reasonable to conclude that the non-specific, passive solvent effect is not a dominating factor in this reaction.

Gawley[2] suggested in his review that in sulfuric acid solution, a sulfate oxime ester could be the effective reactive component rather than the oxime itself. In order to test further this proposal, we have considered the process starting from a protonation of the simplest sulfate ester, $H_2C{=}N{-}OSO_3H$. Selected geometrical parameters of related structures employing HF/6-31G(d) wavefunctions are summarized in Fig. 2, whereas calculated total and relative energies are also recorded in Table 1. Fig. 3 displays the energy profile showing the isomerization and rearrangement in the gas phase of both systems without and with the sulfate substituents. It is clear that involvement of a sulfate oxime ester does not induce a genuine effect on either the rate-controlling 1,2-H-shift or the migration-elimination step. The energy difference between both N- and O-protonated forms remains almost unchanged upon sulfate substitution. SCRF calculations in water continuum ($\varepsilon = 78.3$) using gas phase geometries of the stationary points show again that the non-specific solvent effect is small. Therefore, we have not pursued further studies on this reaction path.

We now turn to the process in which the solvent molecules participate actively in the reaction process. As a simple and treatable model, we have chosen one neutral H_2SO_4 molecule to mimic the specific interaction of concentrated sulfuric acid or

Table 3 Calculated total, zero-point and relative energies (in parentheses, including ZPE corrections) of the considered stationary points, including active solvent effects

Structure[a]	HF 6-31G(d)	MP2 6-311G(d,p)	ZPE[b]
$H_2C{=}NH{-}OH(+) + H_2SO_4$	−867.208 85 (−97)	−868.813 27 (−81)	250
$H_2C{=}NH{-}OH \cdots H_2SO_4$ complex (+) **NS**	−867.242 70 (−184)	−868.853 26 (−183)	252
TS 1,2-H-shift **TS1S**	−867.184 49 (−40)	−868.804 14 (−64)	243
$H_2C{=}NH{-}OH_2 \cdots H_2SO_4$ complex (+) **OS**	−847.206 53 (−95)	−868.823 42 (−112)	246
$H_2C{=}NH{-}OH_2$ (+) + H_2SO_4	−867.169 76 (0)	−868.780 27 (0)	244

[a] Based on HF/6-31G(d) geometries, given in Fig. 3. [b] Based on HF/6-31G(d) vibrational wavenumbers and scaled by 0.9.

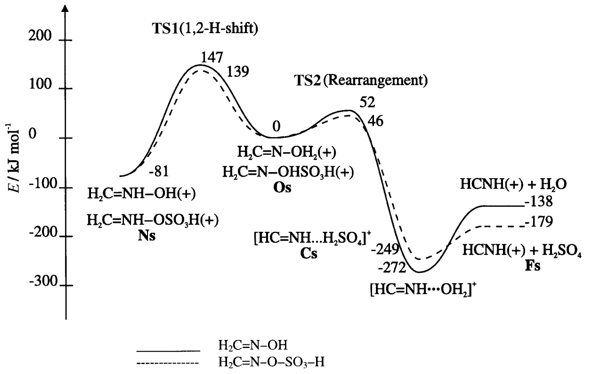


Fig. 3 Schematic energy profile showing the 1.2-H-shift and rearrangement of protonated esters. Values at the MP2/6-311G(d,p)//HF/6-31G(d) + ZPE level.

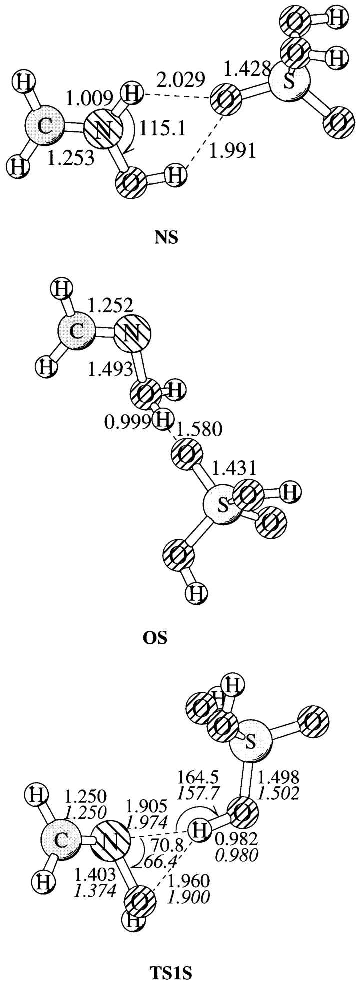


Fig. 4 Main geometrical features of the stationary points including the participation of a H_2SO_4 solvent molecule, both in the gas phase and in solvent ($\varepsilon = 78.3$). The letter **S** stands for H_2SO_4 molecule. Different letter styles (italic, bold) are used to distinguish calculations in the gas phase ($\varepsilon = 1$) and in the solvent ($\varepsilon = 78.3$), at different levels: HF/6-31G(d) geometries in the gas phase; *HF/6-31G(d) geometries in the solvent*.

oleum solvents with the oxime system. Of course, other ionic species such as HSO_4^-, SO_4^{2-}, $HS_2O_7^-$, $H_3SO_4^+$, or an oligomer of solvent molecules are also expected to be present in these solutions and might play a certain role in the reaction. However, we were not able to locate a transition structure including more than one active solvent molecule. Therefore, it seems reasonable to admit that intervention of a second solvent molecule in the BR process is no longer a crucial factor.

Because the 1,2-H-shift connecting both N- and O-protonated oxime forms is the most energy-demanding step, we have only considered the question of how a solvent molecule could modify the course of this step by including it as a co-reactant. Once the O-protonated species is formed, it is rapidly converted to the products either with or without the presence of solvent.

Selected geometrical parameters for critical points of the supersystem including a protonated oxime and a sulfuric acid molecule are given in Fig. 4. The corresponding total and relative energies are listed in Table 3. The essential energetic features of the isomerizations with and without a H_2SO_4 molecule are illustrated in Fig. 5. Owing to the presence of hydrogen atoms, interaction between both solute and solvent molecule leads, as expected, to a number of weak hydrogen-bonded complexes. We have found that the five-membered cyclic complex **NS** (Fig. 4), having hydrogen-bond bridges with intermolecular distances of about 2 Å, is the most stable dimeric form with a complexation energy of 102 kJ mol^{-1} (Mp2/6-311G(d,p) + ZPE). Similarly, a strong complex **OS** between the O-protonated oxime and H_2SO_4 is formed; the corresponding complexation energy turns out to be somewhat larger (122 kJ mol^{-1}), in line with a shorter $O{-}H \cdots O$ intermolecular distance (1.6 Å). Thus, the O-protonated form is more stabilized upon complexation but remains far less stable than its N-counterpart.

The transition structure **TS1S** connecting both complexes **NS** and **OS** shows some remarkable features. Although from a geometrical viewpoint, it looks like a weak interaction between an oxime molecule and a $H_3SO_4^+$ cation, an analysis of its imaginary vibrational mode shows, however, that the transition vector corresponds to a migration of a hydrogen atom between both atoms N and O of the oxime moiety. An intrinsic reaction coordinate calculation (IRC) confirms that in going from one protonated oxime form to the other, the migrating hydrogen is virtually transferred to the H_2SO_4 moiety at the transition state. The $N{-}H \cdots OSO_3H_2$ distance varies from 2.029 Å in **NS** to 0.982 Å in **TS1S**. A similar variation can also be noted for the $O{-}H \cdots OSO_3H_2$ distance. With the presence of a H_2SO_4 molecule, the 1,2-migration thus proceeds through a transition state in which the solvent molecule facilitates the hydrogen migration between both protonated oximes by catching the migrating hydrogen from one end and putting it on the other end. The fact that a hydrogen transfer has effectively taken place in **TS1S** is due to the difference in proton affinity between the oxime and sulfuric acid. Owing to the stabilization through hydrogen transfer, the transition state can now be reached more easily and implies a substantial reduction of the energy barrier, in going indeed from 234 kJ mol^{-1} in the non-assisted system to

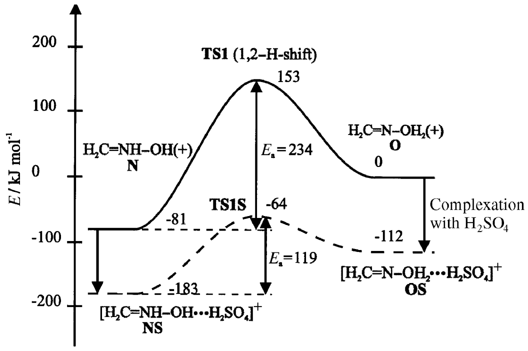


Fig. 5 Schematic energy profile showing the rate-controlling 1,2-H-shift in both gas phase and H_2SO_4 catalysed reaction paths. Energies obtained from MP2/6-311G(d,p) + ZPE calculations. E_a stands for energy barrier.

119 kJ mol^{-1} in the H_2SO_4-assisted system. The latter value approaches more closely to the experimental results for substituted oximes (about 100 kJ mol^{-1}).[4] Overall, it is obvious that the solvent helps the solute to perform the 1,2-H migration by taking place directly in the reacting supermolecule.

Owing to the fact that the solvent molecule is regenerated after the process, it occupies here the role of a catalyst. In this particular case, which involves H-migration, the catalytic action of the solvent simply resides in its capacity to accept a proton; its proton affinity needs to be larger than that of the oxime. Given that sulfuric acid is present in a huge excess with respect to the oxime, the participation of more solvent molecules also seems possible, for example, one of them protonating the oxygen atom and a second one deprotonating the nitrogen atom. Owing to the high computational costs, we have considered this possibility by taking two water molecules instead of two H_2SO_4 molecules. In spite of an extensive search, we were not able to locate a transition structure of that kind; as such, the participation of two active solvent molecules in the reacting supersystem to accelerate the hydrogen transfer is rather doubtful.

It should be stressed that all the searches were performed without consideration of long-range continuum effects. Therefore, we have computed the reaction path of the $[H_2CNH\text{-}OH \cdots H_2SO_4]$ supermolecule within both SCRF and PCM continuum models. Results from single-point calculations, both in the gas phase and in solvent, are given in Table 2 and indicate that electrostatic solvent effects play no significant role in affecting the considered reaction path only slightly. Because a change in the reaction coordinates in the presence of a continuum can reasonably be expected for a proton transfer reaction, we attempted to reoptimize the reaction path in the presence of the solvent reaction field using the Onsager SCRF model. Selected geometrical parameters, both in the gas phase and in solvent ($\varepsilon = 78.3$) are given in Fig. 4.

It turns out that only the 1,2-H-shift transition structure **TS1S**, involving one active H_2SO_4 molecule, could be optimized in solvent. As seen in Fig. 4, when including the solvent reaction field, the transition structure for 1,2-H-shift **TS1S** and its characteristics are, compared to those of the gas phase structures, not modified significantly. Owing to the limitations of the Onsager SCRF model, we were however not able to re-optimize the minima **NS** and **OS** in solvent. Given that the true molecular form of both minima **NS** and **OS** (see Fig. 4) is far from being spherical, most of the cavity considered is empty, which tends to diminish the solvation energy. A more evolved method, the PCM model, involving a cavity of molecular shape would give more accurate results. Unfortunately, since calculations of the energy gradients within the PCM formalism are not yet possible, geometrical parameters cannot be fully optimized using this method. As the transition structure **TS1S** looks more spherical, no practical problems occur at this point in using the Onsager SCRF model. From the available results, it seems plausible to expect that the solvent continuum does not change fundamentally the geometrical parameters of these **NS** and **OS** minima.

Conclusions

This paper reports a theoretical study modelling the Beckmann process in sulfuric acid solution. Whereas the formation of a sulfate ester, $H_2C{=}N{-}O{-}SO_3H$, apparently plays no significant role in affecting marginally the rate-controlling 1,2-H-shift, a specific interaction between a neutral H_2SO_4 molecule and a solute protonated oxime molecule seems to be the dominant factor in reducing substantially the energy barrier to 1,2-H-shift. Using a neutral H_2SO_4 molecule to represent an active solvent participation, MP2/6-311G(d,p) energy calculations based on HF/6-31G(d)-geometries reveal that the barrier associated with the rate-determining 1,2-H-shift is decreased by 115 kJ mol^{-1} with respect to the gas phase value and thereby approaches experimental values. The H_2SO_4 molecule interacts specifically with the migrating hydrogen and thereby assists the migration inducing a hydrogen transfer at the transition state. Although the participation of other charged species, or even $(H_2SO_4)_n$ oligomers, is to be expected in concentrated sulfuric acid solution, we feel confident in suggesting that, in view of the large reduction of the energy barrier, specific interaction of a neutral H_2SO_4 molecule constitutes a realistic model for the BR in related solutions. In the corresponding supersystem, there is apparently no available place for additional solvent molecules in order to carry out the specific action. Overall, our calculations strongly suggest that we are dealing here again with a strong case of active solvent catalysis.[7b]

Acknowledgements

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