SHORT PAPER

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Ab initio study of solvent effects on rate of 1,3-dipolar cycloadditions of benzonitrile oxide and various dipolarophiles

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Ab initio molecular orbital calculations have been used to investigate the structures and the transition states of 1,3-dipolar cycloadditions between benzonitrile oxide with ethylene, cyclopentene, acrylonitrile and tetracyanoethylene in heptane and water: calculations reveal enhanced hydrogen bonding of a water molecule to the transition states for the cycloaddition 1,3-dipolar of reaction of benzonitrile oxide with cyclopentene, the optimal interaction energies being 0.7 kcal/mol more favourable for hydrogen bonding to the oxygen atom in the transition states than for the reactants.

Keywords: *ab initio*, 1,3-dipolar cycloaddition, reaction field, hydrogen bonding, hydrophobic interactions

Water has special effects on chemical reactions. In spite of practical problems such as limited solubility of reactants or the aggressive nature of water toward organic compounds, water is a unique solvent, due to several possible interaction mechanisms: firstly, enhanced hydrophobic interactions because of reduced accessible surface area of the activated complex compared to that of the reactants. Secondly, hydrogen bonding between water molecules and hydrogen bond acceptor groups in a polarisable activated complex. These two effects reduce the Gibbs energy of activation.

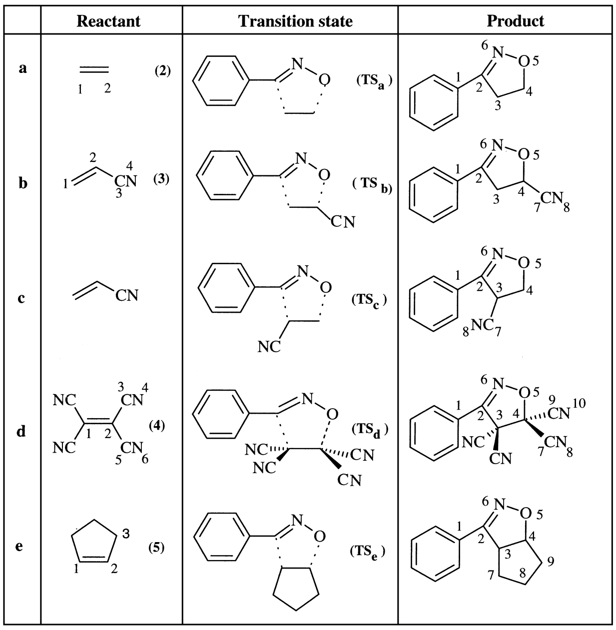
Two reactions of the class of pericyclic reaction, the Claisen rearrangement and particularly the Diels–Alder reaction are the best examples of reactions that benefit from water as the reaction medium.[1-6] Jorgensen and coworkers by combined quantum and statistical mechanics calculations on the Diels–Alder reaction of methyl vinyl ketone and cyclopentadiene product rate accelerations by a factor of 10^3 in aqueous solution over hydrocarbon solvents.[4] Analogous studies also show comparable solvent dependence for the rates of Claisen rearrangements.[4,7]

Solvent effects on another class of pericylic reactions, 1,3-dipolar cycloadditions, have been less well studied. Shiraishi and co-workers reveal that reaction of a nitrile oxide with substituted benzoquinones is slower in dipolar aprotic solvents than in cyclohexane, but there is a rate increase in aqueous ethanol.[8] Reactions of nitrones with a thione or ethyl acrylate show a small, inverse dependence on solvent polarity. Engberts and coworkers found that reaction of phenyl azide and norbornene in a 99:1 mixture of water is 53 times as fast as that in hexane.[9] The reaction rate of 1,3-dipolar cycloaddition of C,N-diphenylnitrone with dibutylfumarate increases remarkable in aqueous solutions relative to other solvents.[10]

Also studies of *ab initio* quantum mechanics and Monte Carlo statistical mechanics on 1,3-dipolar cycloaddition of methyl azide and ethene predicted a rate enhancement in progressing from carbon tetrachloride to the dipolar aprotic solvent DMSO owing to an increase in dipole moment for the transition structure relative to the reactants.[11]

More recently, Engberts and coworkers determined the second-order rate constants for 1,3-dipolarphiles.[12] They reveal that 1,3-dipolar cycloadditions with electron-poor dipolarophiles are accelerated in water and protic solvents, whereas an aqueous medium has no special effect when electron-poor dipolarophiles are involved. In order to compare theoretical studies of solvent effects in 1,3-dipolar cycloadditions with experimental data, we studied the reactions of benzonitrile oxide with acrylonitrile, ethylene, cyclopentene, tetracyanoethylene (Scheme 1) in two solvents. Recently, we studied these reactions in the gas phase.[13]

Reaction with acrylonitrile gives two regioisomeric cycloadducts (**3**,**4**) corresponding to bonding of the oxygen atom at benzonitrile oxide to C1 or C2 in acrylonitrile.



Scheme 1 Reactants, transition states and products in reactions (a-e) of reactants with

Computational methods

The *ab initio* molecular orbital calculations were executed with the GAUSSIAN 98 program[14]. Geometries for all structures were fully optimised by means of analytical energy gradients in restricted Hartree–Fock calculations with the 6-31G* basis set in the solvents of water and heptane.

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†This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Key geometrical parameters for the reactants and transition structures in water[a]

Parameter	1	2	3	4	5	Ts_a	Ts_b	Ts_c	Ts_d	Ts_e
r_{12}	1.45	1.32	1.32	1.34	1.32	1.45	1.46	1.44	1.45	1.45
r_{23}	1.13	-	1.44	1.44	1.51	2.16	2.1	2.35	2.57	2.18
r_{34}	1.24	-	1.14	1.13	1.54	1.36	1.37	1.39	1.47	1.37
r_{45}	-	-	-	-	-	2.15	2.09	1.88	1.54	2.2
r_{56}	-	-	-	1.13	-	1.24	1.23	1.25	1.29	1.24
r_{26}	-	-	-	-	-	1.18	1.18	1.17	1.17	1.18
r_{37}	-	-	-	-	-	-	-	1.43	1.44	1.52
r_{78}	-	-	-	1.13	-	-	1.14	1.14	1.14	1.54
r_{47}	-	-	-	-	-	-	1.44	-	-	-
a_{123}	179.99	-	122.4	121.81	112.23	111.86	113.95	114.72	115.63	111.79
a_{234}	179.99	-	178.6	179.16	-	100.56	101.61	95.01	87.87	100.42
a_{345}	-	-	-	-	-	103.18	102.52	107.87	114.35	100.79
a_{265}	-	-	-	-	-	-	120.79	137.95	137.95	136.73
a_{347}	-	-	-	-	-	-	121.76	118.83	114.79	109.79
a_{489}	-	-	-	-	-	-	-	-	-	-
a_{874}	-	-	-	-	-	-	177.34	-	-	102.92
a_{873}	-	-	-	-	-	-	-	178.66	176.51	102.53
a_{947}	-	-	-	-	-	-	-	-	-	-
a_{523}	-	-	-	116.37	-	-	-	-	-	-

[a] Bond lengths (*r*) in Angstrom, bond angles (*a*) in degrees.

Table 2 Key geometrical parameters for the reactants and transition structures in heptane[a]

Parameter	1	2	3	4	5	Ts_a	Ts_b	Ts_c	Ts_d	Ts_e
r_{12}	1.44	1.32	1.32	1.33	1.32	1.45	1.46	1.45	1.42	1.45
r_{23}	1.13	-	1.44	1.44	1.51	2.17	2.12	2.31	2.52	2.18
r_{34}	1.22	-	1.14	1.13	1.54	1.36	1.37	1.38	1.43	1.37
r_{45}	-	-	-	-	-	2.16	2.12	1.93	1.64	2.21
r_{56}	-	-	-	1.13	-	1.24	1.23	1.25	1.28	1.24
r_{26}	-	-	-	-	-	1.18	1.18	1.17	1.17	1.18
r_{37}	-	-	-	-	-	-	-	1.44	1.44	1.52
r_{78}	-	-	-	1.13	-	-	1.14	1.14	1.13	1.54
r_{47}	-	-	-	-	-	-	1.44	-	-	-
a_{123}	179.99	-	122.2	121.81	112.23	112.81	114.19	114.72	112.95	112.36
a_{234}	179.99	-	179.3	179.16	-	100.48	101.63	96.74	90.3	100.4
a_{345}	-	-	-	-	-	103.15	102.26	106.76	112.19	102.72
a_{265}	-	-	-	-	-	137.09	136.98	137.95	137.95	136.73
a_{347}	-	-	-	-	-	-	120.79	119.79	116.09	102.92
a_{489}	-	-	-	-	-	-	-	-	-	-
a_{874}	-	-	-	-	-	-	177.9	-	-	-
a_{873}	-	-	-	-	-	-	-	178.91	178.53	102.53
a_{947}	-	-	-	-	-	-	-	-	-	-
a_{523}	-	-	-	116.37	-	-	-	-	-	-

[a] Bond lengths (*r*) in Angstrom, bond angles (*a*) in degrees.

Calculations of reaction field were carried out with the Onsager model. In this reaction field model, the solvent is represented by a continuous dielectric characterised by a given dielectric constant (ε). The solute is assumed to be embedded into a spherical cavity with radius a_o, in the medium. The suitable solute radii are computed by a gas phase molecular volume calculation in a separate job step. The energies were computed to the RHF/6-31G* level in each case. The Synchronous Transit-Guided Quasi-Newton (STQN) method was used to locate the transition state structure. Vibrational frequencies were calculated at the RHF/6-31G* level for all reactants and transition states, which were confirmed to have zero and one imaginary frequency respectively. The frequencies were scaled by a factor of 0.8929. Calculations of vibrational frequencies permitted computation of Gibbs free energies of reactants and transition states. The calculated free energies were used for computation of rate constants of reactions in two solvents, water and heptane, by the Eyring equation:

$$k = k_B T/h \exp(-\Delta G^{\neq}/RT)$$

$\Delta G^{\neq}$ is the difference between the free energies of transition state and reactants.

Then optimisations were carried out for complexes of acrylonitrile, benzonitrile oxide and the transition states of reactions of c and e with water molecules. The 6-31G* basis set was chosen for the calculations since it is known to perform particulary well computing the strengths and geometries of hydrogen bonds.

Results and discussion

The key geometrical parameters for the reactants and transition structures in the solvents of water and heptane are recorded in Tables 1 and 2.

These results show that there are insignificant differences between the geometrical parameters in the two solvents.

The free energies derived from the reactants and transition states for each structure in the two solvents are recorded in Table 3. The free energy changes and the rate constants of the 1,3-dipolar cycloadditions of benzonitrile oxide and various dipolarophiles are recorded in Table 4.

Comparing the data of activation free energy changes and rate constants show that the rates of cycloadditions of the 1,3-dipole with electron-poor dipolarophiles are larger than with other dipolarophiles in the two solvents.

Table 3 Free energies (kcal/moal) derived from the reactants and transition states for each structure in water and heptane

Structure	Water	Heptane
Ethylene	-77.9978	-77.9978
Benzonitrile oxide–ethylene	-475.038	-475.038
Acrylonitrile	-169.247	-169.741
Benzonitrile oxide–acrylonitrile (a)	-566.784	-566.777
Benzonitrile oxide–acrylonitrile (b)	-566.787	-566.783
Benzonitrile oxide	-397.126	-397.116
Tetracyanoethylene	-444.9	-444.9
Benzonitrile oxide–tetracyanoethylene	-841.968	-841.953
Cyclopentene	-193.879	-193.879
Benzonitrile oxide–cyclopentene	-590.917	-590.915

Table 4 Free energy changes and rate constants in 1,3-dipolar cycloadditions with benzonitrile oxide as dipolar[a]

Structure	Water		Heptane	
	$\Delta G^{\neq}$	10^{28}K	$\Delta G^{\neq}$	10^{25}K
Ethylene	53.85	1.98×10^{1}	47.9	4.58×10^{2}
Acrylonitrile (a)	55.34	1.6	50.47	5.97
Acrylonitrile (b)	53.35	4.61×10^{1}	42.2	6.94×10^{6}
Tetracyanoethylene	36.33	1.4×10^{14}	39.68	4.89×10^{8}
Cyclopentene	55.35	2.75	50.28	8.23

[a] Free energy changes in kcal/mol and rate constants in l/mol/s.

Table 5 Experimental rate constants for the 1,3-dipolar cycloaddition of benzonitrile oxide with two dipolarophiles[11]

Dipolarophile	10^2 k l/mol/s	
	Water	Heptane
Acrylonitrile	1.1	1.5
Cyclopentene	8.5	2.6

Table 6 Key geometrical parameters for complexes of acrylonitrile(AN),benzonitrile oxide(BO) and transition states of reactions of c and e with water molecules at level RHF/6-31G*[a]

Parameter	AN–H_2O	BO–H_2O	$(CP–BO)_{TS}–H_2O$	$(AN–BO)_{TS}–2\ H_2O$
r_{12}	1.22	1.13	1.25	1.95
r_{23}	2.16	2.25	1.98	2.13
r_{34}	0.94	0.94	0.95	0.95
r_{45}	0.94	0.94	0.94	0.94
r_{67}	-	-	-	1.13
r_{78}	-	-	-	2.18
r_{89}	-	-	-	0.95
r_{910}	-	-	-	0.94
a_{123}	88.27	168.24	112.9	91.83
a_{234}	148.75	168.13	164.43	145.94
a_{345}	105.06	104.78	105.19	106.2
a_{678}	-	-	-	137.25
a_{789}	-	-	-	159.05
a_{8910}	-	-	-	106.13

[a] Bond lengths (*r*) in Angstrom, bond angles (*a*) in degrees.

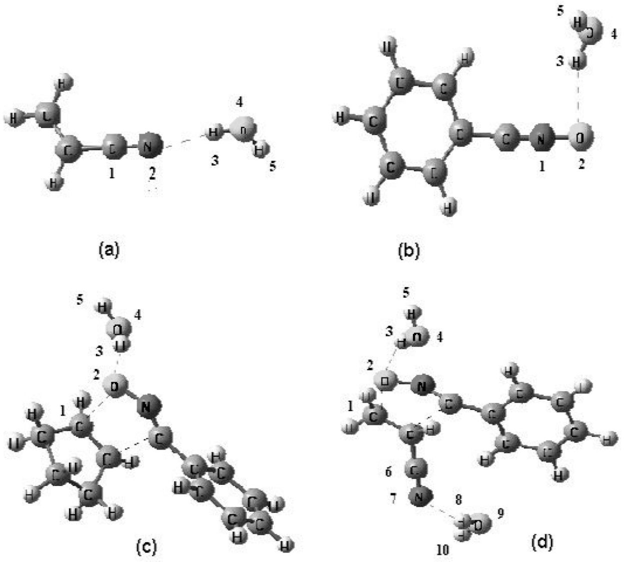

Fig 1 The 6-31G* optimised geometries for complexes of reactants and the transition states in reactions c and e with water molecules.

Comparing rate constants of reactions obtained in the two solvents shows that rates of reaction in heptane are greater than in water.

In contrast to the situation for many Diels–Alder reactions there is not a gain in hydrogen-bond accepting ability for the transition structure of the 1,3-dipolar cycloadditions. Also, the formation of hydrogen bonds with reactants that include polar groups as acrylonitrile and benzonitrile oxide, increases the stability of the reactants and hence decreases reactivity. Thus we expect the rates of these reactions in aqueous solutions to be lower than in organic solutions. Thus we investigated the formation of hydrogen bonding in reactions c and e for better comparing with experimental results.

Experimental rate constants for the 1,3-dipolar cycloaddition of benzonitrile oxide with two dipolarophiles by Engberts and coworkers[11] are given in Table 5.

Results of Tables 4 and 5 show much difference. The discrepancy between the experimental and computed rate constants might suggest the need to progress to larger basis sets with the use of a more exact model of reaction field and this will be an interesting point to pursue in future studies. Also, we considered the effect of the formation of hydrogen bonds for an approach to the experimental results. Thus, we selected two reactions, e and c and investigated the complexes of the reactants and the transition states with water molecules, like the work on the Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone and acrylonitrile of Blake *et al.*[4]

The 6-31G* optimised geometries for the complexes of the reactants and the transition states in reactions c and e with

Table 7 Total energies (au) and binding energies (kcal/mol) for the reactions of C and e[a]

Species	$E_{tot}{}^{b}$	ΔE^{b}	$E_{tot}{}^{c}$	ΔE^{c}	$E_{tot}{}^{d}$	ΔE^{d}	$E_{tot}{}^{e}$	ΔE^{e}
H_2O	−76.0107465		−76.40895		−76.4225862		−76.0346	
AN	−169.7680151		−170.8315507		−170.8403281		−169.783	
AN–H_2O	−245.7856494	−4.32	−247.2486181	−5.09	−247.27058	−4.81	−245.823	−3.64
BO	−397.1923999		−399.6398911		−399.6566522		−397.222	
BO–H2O	−473.2136723	−6.6	−476.0598746	−6.92	−476.0862057	−5.06	−473.263	−3.54
$(AN–BO)_{TS}$	−566.9106723		−570.4508206		−570.473224		−566.951	
$(AN–BO)_{TS}$-H_2O	−718.9537378	−5.1	−723.2946193	−16.25	−723.3370215	−11.69	−719.035	−9.35
CP	−193.9773419		−195.3271381		−195.3345819		−194	
$(CP–BO)_{TS}$	−591.1131712		−594.9445292		−594.9657284		−591.161	
$(CP–BO)_{TS}$-2H_2O	−667.1355362	−7.29	−671.3654054	−7.48	−671.3967324	−5.28	−667.203	−4.85

[a] AN=acrylonitrile, BO = benzonitrile oxide,CP = cyclopentene, Δ*E* is binding energy for the complex relative to the separated molecules. [b] RHF/6-31G*//RHF/6-31G*. [c] B3LYP/6-31G*//B3LYP/6-31G*. [d] B3LYP/6-31G*//B3LYP/6-31++G*. [e] RHF/ 6-31G*//MP2/6-31G*.

Table 8 The optimal interaction energies (OIE) (kcal/mol) for reactions c and e[a]

Reaction	OIE[b]	OIE[c]	OIE[d]	OIE[e]
c	5.82	–4.24	–1.82	–2.17
e	–0.7	–0.56	–0.22	–1.31

[a] $OIE = \Delta E_{TS\text{-}H2O} - \Sigma\, \Delta E_{reactants\text{-}H_2O}$.
[b] RHF/6-31G*//RHF/6-31G*.
[c] B3LYP/6-31G*//B3LYP/6-31G*.
[d] B3LYP/6-31G*//B3LYP/6-31++G*.
[e] RHF/6-31G*//MP2/6-31G*.

water molecules are shown in Fig. 1 and their the key geometrical parameters are recorded in Table 6.

Also, electron correlation calculation were performed at level B3LYP/6-31G* and MP2/6-31G*. The total energies and binding energies from the ab initio RHF/6-31G*, B3LYP/6-31G*, B3LYP/6-31++G* and MP2/6-31G* calculations are recorded in Table 7.

By using these data, we computed the amount of stability or instability of the transition state relative to the reactants in each reaction as follows:

Optimal interaction energy (OIE) = $\Delta E_{TS\text{-}H_2O} - (\Sigma \Delta E_{Reactants\text{-}H_2O})$

These results are recorded in Table 8.

The difference of binding energies between the transition states and the reactants show at level RHF/6-31G*//RHF/6-31G* enhanced hydrogen bonding of water to the transition state in the reaction with cyclopentene and the optimal interaction energies are found to be 0.7 kcal/mol favourable for hydrogen bonding to the oxygen in the transition state than for the reactants, whereas in the cycloaddition with acrylonitrile, the interaction energies were obtained 5.8 kcal/mol more favourable for hydrogen bonding to oxygen or nitrogen in the reactants than the transition state.

Thus we expected the cycloaddition of benzonitrile oxide with cyclopentene to be accelerated in water over organic solutions and for the effect on the cycloaddition of benzo nitrile oxide with acrylonitrile to be reversed. This accords with experimental results.[8]

The calculations at level of B3LYP and MP2 show that the difference at ΔE for complexes of the transition state with water molecules and the reactants with water molecules in reaction c is more negative than in reaction e. This means that unlike the reality, these methods show that the rate of reaction c should be more than reaction e. Just as with the results of Blake et al, mentioned above, good results at level RHF/6-31G* for the Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone and acrylonitrile.[4] This research also shows that calculations at the RHF/6-31G* level have good results in the study of solvent effects on 1,3-dipolar cycloaddition reactions.

An explanation for these results can be as follows: the special effects of water on chemical reactions are due to several interaction mechanisms.[6] In particular hydrophobic interactions, which largely stem from the limited ability of water to dissolve apolar molecules are of importance. Since cycloaddition reactions are characterised by a negative volume of activation, the hydrophobic surface area of the reactants in water is reduced on going from the initial state to the transition state. Therefore, the Gibbs energy of activation is lowered, and the reaction is accelerated. But, the loss of exposed surface area should be similar for most of the cycloaddition reactions. Also, the capacity of water to act as both a hydrogen-bond donor and a hydrogen-bond acceptor can have major effects on chemical transformations.

However, since in the reactants of c and e, only cyclopentene cannot form hydrogen bonding, thus the transition state with cyclopentene should be more stable than that with acrylonitrile in water.

Table 9 The free energies (G) in au for reactants and transition states of reactions c and e[a]

Species	G[b]	G[c]
AN–H_2O	–245.741648	–247.210408
BO–H_2O	–473.11386	–475.969425
$(AN–BO)_{TS}–2H_2O$	–718.782718	–723.137544
CP	–193.879095	–195.237236
$(CP–BO)_{TS}–H_2O$	–666.91625	–671.163608

[a] AN=acrylonitrile, BO = benzonitrile oxide,CP = cyclopentene.
[b] RHF/6-31G*//RHF/6-31G*.
[c] B3LYP/6-31G*//B3LYP/6-31G*.

Table 10 The free activation energies ($\Delta G^{\neq}$) and electronic activation energies ($\Delta E^{\neq}$) in kcal/mol.

Reaction	$\Delta G^{\neq a}$	$\Delta E^{\neq a}$	$\Delta G^{\neq b}$	$\Delta E^{\neq b}$
c	45.67	28.54	26.54	8.7
e	48.13	34.81	27.02	13.56

[a] RHF/6-31G*//RHF/6-31G*.
[b] B3LYP/6-31G*//B3LYP/6-31G*.

Also, the treatment of electron correlation was investigated on electronic activation energies and free activation energies. The results are recorded in Tables 9 and 10.

These results show that the energy barrier for reaction e is more than that for reaction c at levels RHF/6-31G* and B3LYP/6-31G*. Thus, these calculations did not conform with the experimental results.

In order to get accurate results, the use of a more exact model of reaction field as Consistent Isodensity PCM model (SCI-PCM) and also the use of more diffuse and polarization functions is recommended. These calculations are more complex and require very much CPU time for computation.

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