Solvent Influence on the Diels-Alder Reaction Rates of 9-(Hydroxymethyl) anthracene and 9,10-Bis(hydroxymethyl) anthracene with Two Maleimides

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ABSTRACT: The rates of the Diels–Alder reaction of 9-(hydroxymethyl)anthracene and 9,10-bis(hydroxymethyl)anthracene with maleic anhydride and two maleimides, N-ethyl- and N-phenylmaleimide, have been studied at various temperatures and pressures in different solvent media. A rate acceleration in water in comparison with organic solvents is observed. Thermodynamic functions of activation for the reaction of 9,10-bis(hydroxymethyl)anthracene with N-ethylmaleimide in binary 1,4-dioxane–water mixtures are determined. From the observed tendencies, it can be concluded that acceleration of the Diels–Alder reactions in water is linked with an energetically favorable dehydration of the reaction centers of the reactants on the way to the activated complex. Addition of an organic cosolvent makes the desolvation of these centers less favorable. © 2016 Wiley Periodicals, Inc. Int J Chem Kinet 49: 61–68, 2017

INTRODUCTION

There are several ways to increase the rate of Diels–Alder reactions (DAR) [1]. The formation of strong *n*,

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v-complexes between the Lewis acids and dienophiles increases the reaction rate by up to 6 orders of magnitude without changing the equilibrium constants [1,2]. Carrying out cycloaddition reactions under high external pressure leads to an increase of both their rate and equilibrium constants [1,3]. Changing the solvent can also influence the rate constants. Unlike organic solvents, until recently the reactions in water had no practical use because of the low solubility of reactants and products. However, observations of unexpected accelerations of the nonpolar DARs in water in comparison with organic solvents have arisen a considerable interest to this solvent because of its availability and the nature of the acceleration effect [4–12].

Currently many types of reactions with significant rate increases in water are known [13]. Novel methods of further acceleration and alteration of selectivity of these reactions have been developed. For example, DARs of inert aromatic compounds were accelerated in water by placing them into self-assembled coordination cages [12]. New microfluidic devices allow to facilitate molecules to come to and to be removed from aqueous–organic interfaces, creating a quasi-homogeneous medium [14,15]. A number of heterogeneous reactions "on water" with rapid stirring in aqueous suspensions and emulsions proceed faster than in pure organic solvents and even faster than under homogeneous solvent-free conditions [16]. Some of these processes are effective combinations of click-chemistry and green-chemistry approaches [17]. Such an increase in the rate of heterogeneous reactions "on water" with rapid stirring is likely to be driven by the strong interactions at the interface between water and hydrophobic reactants [18].

The effects of hydrophobic promotion [4,10,11], the influence of the solvent's cohesive energy [19], and a sharp rise in the energy level of the reactants in comparison with a smaller rise of the energy of the activated complex [10,11] have been named as possible causes of the rate acceleration in water. Accumulation of the kinetic data allows to clarify the mechanism of homogeneous reactions "in water" and heterogeneous reactions "on water" [20]. The extensive studies of the DAR of 9-(hydroxymethyl)anthracene (**1**) with *N*-ethylmaleimide in water, in the presence of inorganic salts, and in binary aqueous–organic solvents have been carried out [4–11]. **1** is a good choice as diene to study the hydrophobic promotion due to its large hydrophobic surface. Its aqueous solubility is only about 10^{-4} mol·L^{-1}. However, it is sufficient for UV/vis spectrophotometric monitoring of the reaction rate thanks to its high UV light absorption coefficient. Most of the dienophiles having heteroatomic activating groups are better soluble in water than dienes.

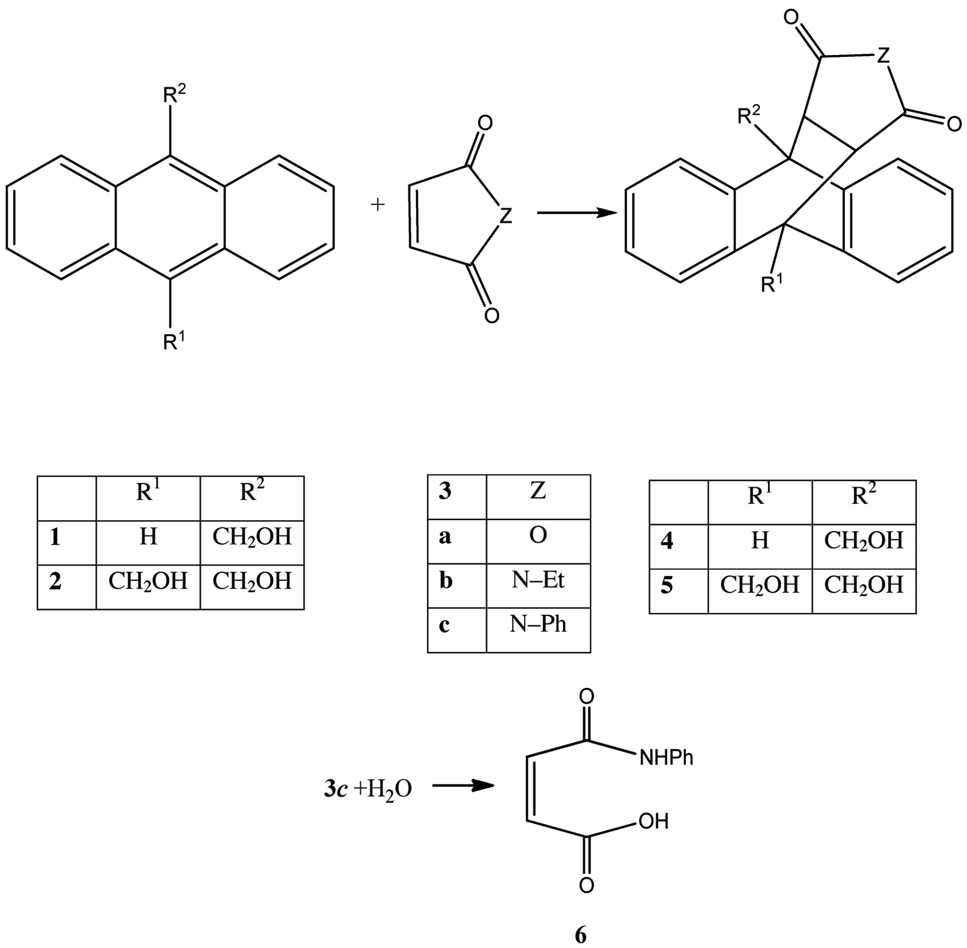
Hydrogen-bond formation between reactants and water can also be one of the reasons for the reaction rate enhancement in water. On the other hand, it has been noted that 2,2,2-trifluoroethanol forms stronger H bonds than water, but the reaction rate of **1** with *N*-ethylmaleimide in water is almost 60 times higher than that found in 2,2,2-trifluoroethanol [10,11].

In fact, many explanations of the solvent-induced rate acceleration can be reduced to the same physical basis. The relative strength of interactions between the reactants and solvent in comparison with the strength of solvent–solvent interactions is governing the reaction rates. In all DARs in solution, it is always necessary to remove some solvent (S) molecules surrounding the reaction centers of diene and dienophile before they form an activated complex (Eq. (1)):

$$\begin{aligned}&(\text{Diene})\cdot \mathrm{S}_n + (\text{Dienophile})\cdot \mathrm{S}_m\\ &\quad\rightarrow (\text{Activated complex})^{\neq}\cdot \mathrm{S}_p + \mathrm{S}_{(n+m-p)} \qquad (1)\end{aligned}$$

If the energy of interactions of reactants with the solvent is higher than the solvent–solvent interaction energy, it will be difficult to desolvate the reactants and the reaction rate will be reduced [21,22]. The rates of DARs will be increased in two cases: (1) the solvent is rather *weakly* interacting with the reactants, and formation of the activated complex is accompanied by an *easy* desolvation followed by formation of *strong* intermolecular solvent–solvent interactions, which is the case for hydrophobic reactants in water; (2) *weak* interactions of reactants with solvents such as alkanes and perfluoroalkanes, when the activated complex formation is accompanied by an *easy* release of the solvent molecules with subsequent formation of *weak* solvent–solvent interactions (S–S). In solutions in alkanes and, especially, in perfluoroalkanes, intermolecular interactions of diene–dienophile couples are generally stronger than those between solvent molecules [23]. Therefore, in both cases an increase in the DAR rate can be expected, but this effect is stronger in water.

In this work, we study and compare the influence of organic and binary aqueous–organic solvents containing 1,4-dioxane as a cosolvent on the rates of the Diels–Alder reactions of **1** with *N*-phenylmaleimide (**3e**) as well as 9,10-bis(hydroxymethyl)anthracene (**2**) with maleic anhydride (**3a**) and *N*-ethylmaleimide (**3b**) (Scheme 1).



	R^1	R^2
1	H	CH_2OH
2	CH_2OH	CH_2OH

3	Z
a	O
b	N–Et
c	N–Ph

	R^1	R^2
4	H	CH_2OH
5	CH_2OH	CH_2OH

Scheme 1 Reactants and products of the studied DAR.

EXPERIMENTAL

Materials

1 (97%; Aldrich, St. Louis, MO, USA) was recrystallized from benzene (mp 161–162ºC (lit. [24] 159–161ºC)). The purity of **1** (99%) was determined by titration using the fast reaction with the red solution of freshly sublimed 4-phenyl-1,2,4-triazoline-3,5-dione in 1,2-dichloroethane (monitored at 550 nm). **2** was obtained by the known method [25] (mp 285ºC (decomp.) (lit. [25] 287–290ºC)). The concentration of the diene **1** solution was determined from the known value of the absorption coefficient of **1** in water ($\varepsilon = 9400\ \text{cm}^{-1}\cdot\text{M}^{-1}$, $\lambda = 366$ nm) [25] and that of **2** using the corresponding value in 1,4-dioxane ($\varepsilon = 9550\ \text{cm}^{-1}\cdot\text{M}^{-1}$, $\lambda = 393$ nm) [26]. Maleic anhydride (**3a**) was purified by recondensation at 100°C and 100 Pa. ^{1}H and ^{13}C NMR data in solution and the X-ray crystals of **5a** were described [27]. Dienophiles **3b** (99%; Acros Organics, Geel, Belgium) and **3c** (99%; Aldrich) were used as purchased. The solvents were purified by known methods [28].

Kinetic Measurements

The rate of reactions at ambient pressure was monitored according to the change in the UV absorption of dienes **1** or **2** (366–393 nm; spectrophotometer Hitachi U–2800, Tokyo, Japan), the concentrations (ca. 1×10^{-4} mol·L^{-1}) were 30–50 times less than that of dienophiles **3a–c**. The quartz cell (1 cm) was filled with the reagents solution, sealed with a glass stopper, and placed in the thermoblock (±0.1°C) of the cell compartment.

The rate of reaction **2** + **3a** → **5a** at elevated hydrostatic pressure was registered using the UV/vis spectrophotometer (SCINCO, Seoul, South Korea) by the change of the diene **2** absorption; the concentration of which in acetonitrile solution was ca. 3×10^{-4} mol·L^{-1}. The quartz cell (0.4 cm) of variable volume with the reagent solution was placed in a stainless steel bomb with sapphire windows and fixed in the cell compartment of the spectrophotometer "SCINCO." High pressure was created by the multiplier with distilled water as the pressure-transmitting liquid.

In water and aqueous solutions, reagents **1**, **2**, and **3b** are stable but dienophile **3c** slowly hydrolyzes with formation of the amido acid **6** [29]. Despite the presence of two hydroxyl groups in diene **2**, its solubility in water at room temperature was unexpectedly low (ca. 1×10^{-5} mol·L^{-1}). The X-ray structure of crystals of **2** shows associates formed through strong intermolecular hydrogen bonds, which is a likely reason of its low solubility and very low dissolution rate. Owing to this, the saturation limit of diene **2** was obtained by 20-h refluxing, followed by cooling down to the experimental temperature. The absence of changes in concentration of diene **5** in aqueous solutions within 2–3 h was checked before the kinetic measurements. The rate constant of reaction **1** + **3c** → **4c** was calculated from Eq. (2):

$$k_2 \cdot t \cdot c_{\mathbf{3c}} = \ln(D_{1,t=0}/D_{1,t}) \tag{2}$$

Here $c_{\mathbf{3c}}$ is the dienophile **3c** concentration, $D_{\mathbf{1},t=0}$ and $D_{\mathbf{1},t}$ are the initial and current (at time *t*) optical density of diene **1**. Since two parallel reactions occur in the aqueous solution, **3c** + **1** → **4c** and **3c** + **H$_2$O** → **6**, the rate constant of the reaction **3c** + **H$_2$O** → **6** should be determined to find the true rate constant for the first reaction. These data were obtained from the changes in absorption of **3c** in water at 45°C at 295 nm, and the obtained rate constant of **3c** hydrolysis is equal to 1.2×10^{-6} mol·L^{-1}·s^{-1}. The rate constant of reaction **1** + **3c** → **4c** in water at 45°C was calculated taking into account the change of $c_{\mathbf{3c}}$ with time due to hydrolysis of **3c**. In calculations, it has been assumed that reaction **1** + **6** can be neglected. In nonaqueous solutions, reaction **1** + **3c** → **4c** proceeds without side reactions.

RESULTS AND DISCUSSION

Kinetics of the DARs in Pure Solvents

The kinetic data for reaction **1** + **3c** → **4c** in pure solvents are shown in Table I, together with previously reported data for reaction **1** + **3b** → **4b**. The confidence intervals of the rate constants are given for 95% confidence level.

From these results, it follows that the reaction rates of diene **1** with *N*-phenylmaleimide (**3c**) are very close to those observed with *N*-ethylmaleimide (**3b**).

There are no literature data on the reactivity of **2** in the DAR. Table II shows the kinetic parameters for reaction **2** + **3a** → **5a** in four solvents. Thermodynamic functions of activation were determined by fitting of the rate constants to the Eyring equation using the errors-in-variables model to take into account the uncertainty in temperature (0.1 K). The confidence intervals are given for 95% confidence level. From these data, it follows that the reactivity of 9,10-bis(hydroxymethyl)anthracene is comparable to that of 9,10-diethylanthracene and only one order of magnitude less than that of 9,10-dimethylanthracene.

The activation volume of reaction **2** + **3a** → **5a** was calculated using the dependence of the reaction rate from external pressure (Table III).

The data obtained are described by Eq. (3):

$$\ln(k_\mathrm{p}/k_{\mathrm{p}=1}) = 29.92 \ln[(30483 + P)/30483],$$
$$r^2 = 0.9961; n = 7 \tag{3}$$

The activation volume ($\Delta V^{\neq}{}_{\mathrm{exp}}$ = –24.3 ± 1.1 cm^3·mol^{-1}) at atmospheric pressure was calculated

Table I Rate Constants k_2 (L·mol^{-1}·s^{-1}) for the Reaction of **1** with N-ethylmaleimide (**1**+**3b** → **4b**) and N-phenylmaleimide **1**+**3c** → **4c**, and the Ratio of the Rate Constants Measured in Water and Four Organic Solvents ($k_\mathrm{W}/k_\mathrm{S}$) at 45°C

	1 + **3b** → **4b**[a]		**1** + **3c** → **4c**[b]	
Solvent	k_2	$k_\mathrm{W}/k_\mathrm{S}$	k_2[c]	$k_\mathrm{W}/k_\mathrm{S}$
Water	0.226; 0.212[d]	1	0.174 ± 0.004 (5)	1
Acetonitrile	1.07×10^{-3}	211	$(1.53 \pm 0.03) \times 10^{-3}$ (2)	114
n–Butanol	6.66×10^{-3}; $6.77 \times 10^{-3\mathrm{d}}$	34	$(7.27 \pm 0.03) \times 10^{-3}$ (3)	24
Trichloromethane	–	–	$(3.41 \pm 0.05) \times 10^{-3}$ (2)	51
1,4–Dioxane	–	–	$(1.59 \pm 0.03) \times 10^{-3}$ (3)	109

[a] From 4. [b] This work. [c] Number of repeated measurements is given in parentheses. [d] From 30.

Table II Rate Constants k_2 (L·mol^{-1}·s^{-1}), Enthalpies $\Delta H^{\neq}$ (kJ·mol^{-1}), Entropies $\Delta S^{\neq}$ (J·mol^{-1}·K^{-1}), and Free Energies of Activation $\Delta G^{\neq}$ (kJ·mol^{-1}) of the DAR of **2** with Maleic Anhydride (**3a**) Determined in Four Solvents

Solvent	T (°C)	k_2	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
1,4–Dioxane	25	$(1.49 \pm 0.01) \times 10^{-3}$ 0.0120^{a} 0.00148^{b}	48.7 ± 1.5 41.0^{a}	-135.7 ± 4.9 -144^{a}	89.1 ± 2.9 83.9^{a}
	35	$(2.99 \pm 0.02) \times 10^{-3}$			
	45	$(5.42 \pm 0.05) \times 10^{-3}$			
Acetonitrile	25	$(1.76 \pm 0.01) \times 10^{-3}$ 0.0244^{a}	48.4 ± 1.6 36.0^{a}	-135.3 ± 5.2 -155^{a}	88.7 ± 3.1 82.2^{a}
	35	$(3.53 \pm 0.03) \times 10^{-3}$			
	45	$(6.31 \pm 0.07) \times 10^{-3}$			
Trichloromethane	25	$(2.18 \pm 0.02) \times 10^{-3}$ 0.070^{a}	44.3 ± 1.1 31.8^{a}	-147.1 ± 3.4 -160^{a}	88.2 ± 2.1 79.5^{a}
	35	$(4.12 \pm 0.04) \times 10^{-3}$			
	45	$(7.15 \pm 0.07) \times 10^{-3}$			
Toluene	25	$(2.32 \pm 0.02) \times 10^{-3}$ 0.0192^{a}	46.7 ± 4.6 37.7^{a}	-138.5 ± 15 -150^{a}	88.0 ± 9.1 82.4^{a}
	35	$(4.89 \pm 0.04) \times 10^{-3}$			
	45	$(8.07 \pm 0.07) \times 10^{-3}$			

[a] For reaction of **3a** with 9,10-dimethylanthracene [31]. [b] For reaction of **3a** with 9,10-diethylanthracene [31].

Table III The Influence of Pressure, P (bar), on the Rate Constant k_2 (L·mol^{-1}·s^{-1}) of the DAR of **2** with Maleic Anhydride (**3a**) in Acetonitrile at 25°C

P	$k_p/k_{p=1}$	$\ln(k_p/k_{p=1})$
1	1	0
297	1.24	0.219
587	1.90	0.643
905	2.48	0.909
1225	3.10	1.131
1415	3.78	1.331
1772	5.56	1.717

from the following relationship (4):

$$[\partial \ln(k_p/k_{p=1})/\partial P]_{P=1} = -\Delta V^{\neq}_{\text{exp}}/RT = 29.92/30484 \tag{4}$$

The corrected value of the activation volume ($\Delta V^{\neq}{}_{\text{corr}}$ = –21.5 ± 1.1 cm^3·mol^{-1}) was found by taking into account the changes of the reactant concentrations upon compression of the solvent under pressure [22,32], according to Eq. (5):

$$\Delta V^{\neq}_{\text{corr}} = \Delta V^{\neq}_{\text{exp}} + (n-1)\cdot\beta\cdot R\cdot T \tag{5}$$

Here n is the reaction order, β is the compressibility factor of acetonitrile (1.13 × 10^{-4} bar^{-1} [33]), R is the gas constant (83.14 cm^3·bar·mol^{-1}·K^{-1}), T = 298 K. For the DAR with substituted anthracenes, small values of the activation volume are usually observed [1,3,22,34]. For example, for the reaction of maleic anhydride with 9,10-dimethylanthracene and with 9-phenylanthracene in toluene at 25°C the values of $\Delta V^{\neq}{}_{\text{corr}}$ are equal to –19.7 ± 0.8 and –19.6 ± 0.7 cm^3·mol^{-1}, respectively [34].

Kinetics of DAR in 1,4-Dioxane–Water Mixture

The results of kinetic measurements of reaction **2** + **3b** → **5b** in binary 1,4-dioxane–water mixtures are summarized in Table IV.

It should be noted that with an increase of the water mole fraction in binary 1,4-dioxane–water binary mixture, a steady decrease is observed only for the free energy of activation of reaction **2** + **3b** → **5b** (Fig. 1). Both the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation show only small changes for the mixtures below 50 mol% of water, then a decrease, reaching their minima at about 95 mol% of water, and finally start to increase. These dependences are similar to those previously observed for the DAR of 5-hydroxynaphthoquinone with cyclopentadiene in 1-propanol–water mixtures [10].

Interestingly, the dependences of the thermodynamic functions of activation on the solvent composition show similarity in their shape to the typical dependences of the thermodynamic functions of solvation of hydrocarbons (as well as many compounds containing

Table IV The Rate Constants, k_2 (L·mol^{-1}·s^{-1}), Enthalpies, $\Delta H^{\neq}$ (kJ·mol^{-1}), Entropies, $\Delta S^{\neq}$ (J·mol^{-1}·K^{-1}), and Free Energies of Activation, $\Delta G^{\neq}$/(kJ·mol^{-1}), of the Reaction of **2** with N-ethylmaleimide (**3b**) in Binary 1,4-dioxane – Water Mixtures

% H_2O (v/v)	x(H2O)	k_{25}	k_{35}	k_{45}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
0	0	$(4.07 \pm 0.04) \times 10^{-3}$	$(7.90 \pm 0.08) \times 10^{-3}$	$(1.38 \pm 0.02) \times 10^{-2}$	46.0 ± 1.6	-136.3 ± 5.3	86.6 ± 3.2
20	0.542	$(7.57 \pm 0.07) \times 10^{-3}$	$(1.50 \pm 0.01) \times 10^{-2}$	$(2.52 \pm 0.03) \times 10^{-2}$	45.6 ± 3.6	-132.4 ± 11.6	85.1 ± 7.0
40	0.759	$(1.57 \pm 0.01) \times 10^{-2}$	$(2.80 \pm 0.02) \times 10^{-2}$	$(4.67 \pm 0.04) \times 10^{-2}$	40.6 ± 0.7	-143.4 ± 2.4	83.3 ± 1.5
60	0.877	$(3.76 \pm 0.04) \times 10^{-2}$	$(5.96 \pm 0.06) \times 10^{-2}$	$(9.78 \pm 0.10) \times 10^{-2}$	35.1 ± 1.5	-154.4 ± 5.0	81.2 ± 3.0
70	0.917	$(5.89 \pm 0.06) \times 10^{-2}$	$(9.62 \pm 0.09) \times 10^{-2}$	0.145 ± 0.001	32.8 ± 1.1	-158.5 ± 3.5	80.0 ± 2.2
80	0.950	$(8.63 \pm 0.08) \times 10^{-2}$	0.134 ± 0.001	0.200 ± 0.002	30.6 ± 0.4	-162.6 ± 1.1	79.1 ± 0.7
90	0.977	0.189 ± 0.002	0.292 ± 0.003	0.459 ± 0.005	32.4 ± 1.1	-150.2 ± 3.5	77.2 ± 2.1
100	1	0.254 ± 0.003	0.429 ± 0.005	0.636 ± 0.007	33.6 ± 2.2	-143.5 ± 7.2	76.4 ± 4.4

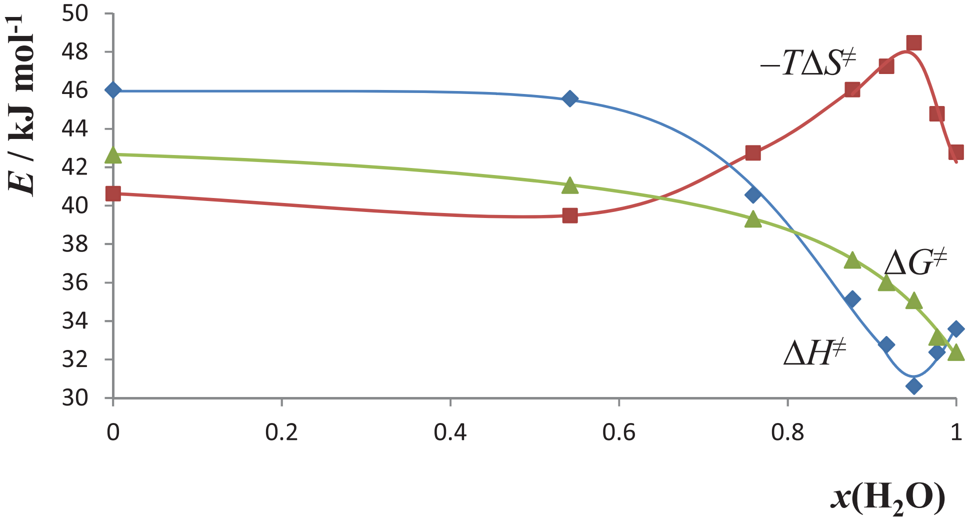


Figure 1 Activation parameters (25°C) for the DAR **2** + **3b** → **5b** as functions of the mole fraction of water in its mixtures with 1,4-dioxane: $\Delta H^{\neq}$ (♦), $-T\Delta S^{\neq}$ (■), and $\Delta G^{\neq}$ (▲). The values of $\Delta G^{\neq}$ have been shifted downwards by 44 kJ·mol^{-1}.

polar fragments) in the mixtures of water with various organic solvents [35] taken with the opposite sign. This speaks in favor of conclusion that the solvent influence on the reaction rates is governed by partial desolvation of the reactants. For example, a maximum of the enthalpies of solvation is also observed in water-rich mixtures. In Fig. 2, the enthalpies of solvation of aniline, benzene, and nitrobenzene [36] in binary 1,4-dioxane–water mixtures are plotted against the solvent composition. The maxima of the enthalpies correspond to 90–93 mol% of water for all three compounds.

At high concentrations of water, the rate constants start to grow up very rapidly with a further increase of the water content. In the range of molar fractions of water between 0.95 and 1, the ratio k_W/k_S increases almost four times due to the favorable change in the entropy of activation. In contrast, at lower concentrations of water the increase of the rate constants is preferably of enthalpic nature.

CONCLUSIONS

From the data obtained, it follows that *N*-ethyl- and *N*-phenylmaleimide are quite similar in their activity as well as from the point of view of a water-induced acceleration of the DAR. Despite the presence of two hydrophilic OH-groups in **2**, its solubility in water is almost 10 times less than that of **1**.

The acceleration effect of the DAR in water is unlikely to be attributed only to the formation of hydrogen bonds between water and reactants [37]. The acceleration effects in the DARs with various dienophiles with different activating groups, capable of forming

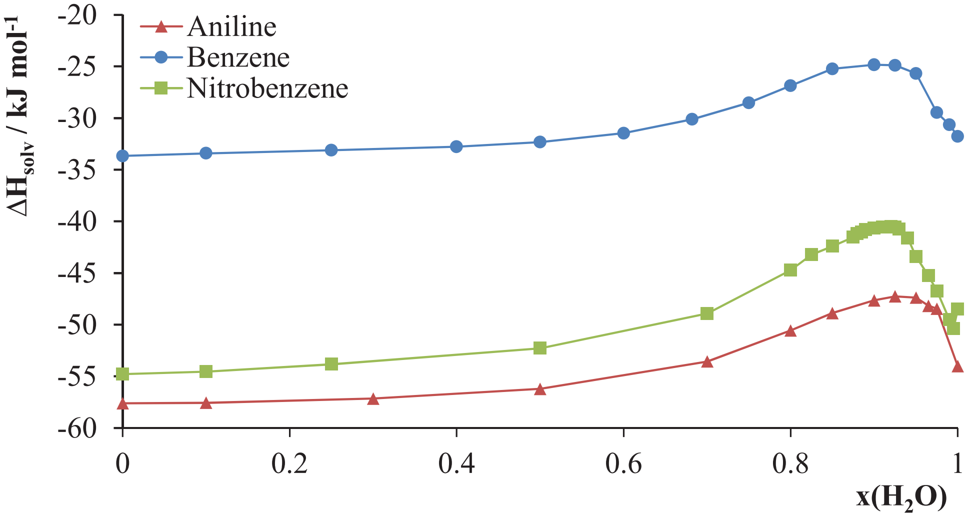


Figure 2 Standard enthalpies of solvation (25°C) of benzene, ethyl acetate, and phenacetin as functions of the mole fraction of water in its mixtures with 1,4-dioxane.

hydrogen bonds with water, are largely dependent on the molecular structure of the dienes [9,16,20,37]. One should take into account that partial dehydration of the reaction centers on the way to the activated complex is accompanied by a large gain in energy due to the favorable water–water interaction (Eq. (1)). Thus, there is a strong acceleration of DARs even between reactants incapable of hydrogen bonding with water. Removal of organic solvent molecules from the solvation shell is much less profitable. Addition of relatively small amounts of organic cosolvents rapidly reduces the rate of DARs in a similar manner as it increases the solubility of apolar reactants. Moreover, the enthalpies and entropies of activation in 1,4-dioxane–water mixture show minima in the mixtures containing about 5 mol% of organic cosolvent, which is likely to be due to desolvation processes.

For the first time, the rates of DAR with 9,10-bis(hydroxymethyl)anthracene have been determined, which allows us to set up an order of activities for 9,10-substituted anthracenes according to the following order: 9,10-dimethyl > 9,10-bis(hydroxymethyl) ≈ 9,10-diethyl > 9-methyl > 9-(hydroxymethyl).

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