CHEMICAL KINETICS
AND CATALYSIS

Effect of Hydrostatic Pressure, Temperature, and Solvent on the Rate of the Diels−Alder Reaction between 9,10-Anthracenedimethanol and Maleic Anhydride

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Abstract—The rate of the reaction between 9,10-anthracenedimethanol and maleic anhydride in 1,4-dioxane, acetonitrile, trichloromethane, and toluene is studied at 25, 35, 45°C in the pressure range of 1−1772 bar. The rate constants, enthalpies, entropies and activation volumes are determined. It is shown that the rate of reaction with 9,10-anthracenedimethanol is approximately one order of magnitude higher than with 9-anthracenemethanol.

INTRODUCTION

The increased attention given to the unexpected acceleration of the Diels−Alder reaction (DAR) in water in comparison to organic solvents is due to both the solvent's accessibility, and to the unexamined nature of the acceleration effect itself [1−9]. There are currently many types of reactions whose rates grow substantially in water [10]. New ways of accelerating and changing the selectivity of reactions have been described using the hydrophobic cavities of created traps into which reagents are forced as in reservations by the hydrophobic effect [9]. However, reactions showing increased rates in water generally have no practical use because of the low solubility and very low concentrations of reactants and products. Unexpected new ways of removing molecules from the surfaces of crystals in water have recently appeared that create pseudo-homogeneous media [11, 12].

Several heterophase cycloaddition reactions proceed faster in water under rapid stirring than in solutions in organic solvents, and even faster than in solutions of reactants without solvents [13]. These processes are effective combinations of fast and environmentally friendly reactions (click-chemistry and green-chemistry) [14]. The sudden increase in the rate of heterophase reactions in water upon rapid stirring is probably due to the strong activation of reagents at the water−hydrophobic reagent interfaces [15]. The effects of hydrophobic aggregation [1], cohesive energy [16], and the sharp rise in the energy level of reactants upon the smaller rise for the activated complex of reactions in water have also been considered as possible causes of acceleration [7, 8]. The unusually high acceleration effects of cyclopentadiene dimerization in water are probably due to the reaction between cyclopentadiene molecules collected in microdroplets providing local concentrations, as in a pure reagent [1].

Extensive studies have been performed for the rate of the DAR between 9-anthracenemethanol and *N*-ethylmaleimide in water, aqueous salt solutions, and common organic solvents [1−8]. The choice of 9-anthracenemethanol as the diene is due to its large hydrophobic surface. The solubility in water of this substance is low (about 10^{-4} M) but sufficient for spectrophotometric monitoring of the reaction rate, due to the high absorption coefficient of the diene. Most dienophiles with heteroatomic activating groups dissolve in water better than dienes.

DARs mostly occur faster in chloroform, due to the activation of dienophiles as a result of the formation of H-bonds [17−21]. Note that 2,2,2-trifluoroethanol forms stronger H-bonds than water, but the rate of the reaction between 9-anthracenemethanol and *N*-ethylmaleimide in water is almost 60 times higher than in 2,2,2-trifluoroethanol [7, 8].

In [22], we showed that the rate of the DAR between *N*-phenylmaleimide and anthracenemethanol in 1,4-dioxane (1.59×10^{-3}) slows slightly, compared to 9-methylanthracene (2.14×10^{-3} L mol^{-1} s^{-1},

Table 1. 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 between 9,10-anthracenedimethanol and maleic anhydride in a number of solvents

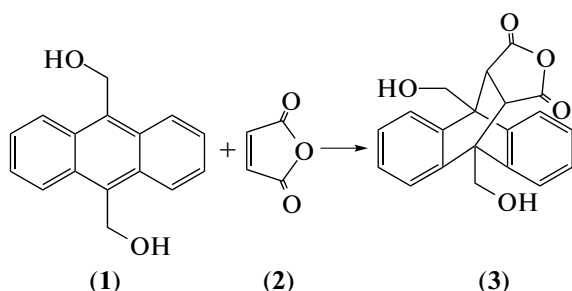| Solvent	T,°C	k_2	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
1,4-Dioxane	25	0.00149	48.6	−136	91.8
		0.0120[a]	41.0[a]	−144[a]	83.9[a]
		0.00148[b]			
	35	0.00299			
	45	0.00542			
Acetonitrile	25	0.00176	47.9	−137	91.5
		0.0244[a]	36.0[a]	−155[a]	82.2[a]
	35	0.00353			
	45	0.00631			
Chloroform	25	0.00218	44.4	−147	91.1
		0.070[a]	31.8[a]	−160[a]	79.5[a]
	35	0.00412			
	45	0.00715			
Toluene	25	0.00232	46.8	−138	90.6
		0.0192[a]	37.7[a]	−150[a]	82.4[a]
	35	0.00489			
	45	0.00807			

[a] Data for the reaction with 9,10-dimethylanthracene [23].
[b] Data for the reaction with 9,10-diethylanthracene [23].

45°C). It is known that 9,10-dimethylanthracene exhibits enhanced activity in the DAR, compared to other dienes [17, 18, 23]. We would therefore expect that 9,10-anthracenedimethanol is more active than 9-anthracenemethanol, expanding the range of reactions with its participation.

In this work, we obtained first data on the rate of the DAR between 9,10-anthracenedimethanol and maleic anhydride in a number of solvents in the given range of temperatures and pressures.

EXPERIMENTAL

We prepared our 9,10-anthracenedimethanol (**1**) using the procedure described in [24]. Maleic anhydride (**2**) was purified by sublimation at 100°C and 100 Pa. Reaction **1** + **2** → **3** proceeded quantitatively.

(**1**)   (**2**)   (**3**)

Data on ^{1}H NMR and ^{13}C in solution, and the XRD of the adduct crystals (**3**) were given in [25]. Solvents were purified according to the familiar procedures in [26]. The reaction rate at ambient pressure was traced (HITACHI U-2900 spectrophotometer) according to the change in the absorption of diene **1**, whose concentration (10^{-4} mol L^{-1}) was 30−50 times lower than dienophile **2**. A closed quartz cuvette (1 cm) containing the solution of reagents was placed into a box (±0.1°C) located in the cell holder.

We also tracked the reaction rate at the elevated hydrostatic pressure (SCINCO S-3100 spectrophotometer) according to the change in the absorption of diene **1**, whose concentration in acetonitrile, $(3-4) \times 10^{-4}$ mol L^{-1}, was 25−30 times lower than that of dienophile **2**. A quartz cuvette (0.4 cm) with variable volume containing the solution of reagents was placed into a bomb of stainless steel with sapphire windows, fixed in the cell holder of Scinco spectrophotometer. High pressure was created with an intensifier (9 : 1) by the pumping of distilled water. The thermal relaxation time after raising the pressure was 3−5 min.
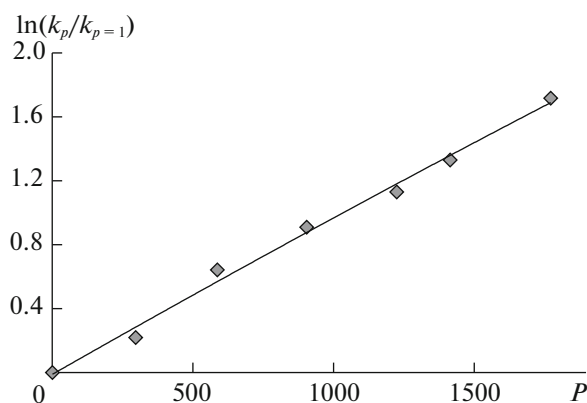
RESULTS AND DISCUSSION

Data from our kinetic measurements for the DAR between 9,10-anthracenedimethanol and maleic anhydride in the given temperature range and in a number of solvents are presented in Table 1.

The approximately 1000% reduction in the reaction rate upon moving from 9,10-dimethylanthracene to 9,10-anthracenedimethanol is like the one observed upon transitioning to 9,10-diethylanthracene (Table 1). As follows from the XRD data, the adjacent 1,8 and 4,5 H-atoms of anthracene eject OH fragments of CH$_2$OH-substituents from the anthracene plane [25], blocking the access of dienophile.

DARs in chloroform generally proceed faster due to the activation of dienophiles upon the formation of H-bonds. In the reaction between maleic anhydride and 9,10-anthracenedimethanol, the formation of

Table 2. Effect of pressure (P, bar) on the rate (k_2, L mol^{-1} s^{-1}) of the Diels−Alder reaction between 9,10-anthracenedimethanol and maleic anhydride 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

Dependence of the rate [$\ln(k_p/k_{p=1})$] of the Diels–Alder reaction between 9,10-anthracenedimethanol and maleic anhydride in acetonitrile at 25°C on the external hydrostatic pressure (P, bar).

hydrogen bonds occurs with both reactants, activating dienophile and deactivating diene, which compensates for the acceleration effect (Table 1). Data on the effect external pressure has on the reaction rate are summarized in Table 2.

The observed value of the activation volume ($\Delta V_{exp}^{\neq}$) is calculated from the dependence $\ln(k_p/k_{p=1})$ vs. P (see figure).

This dependence can be described using the equation for a parabola, and with the logarithmic equation proposed in [21]:

$$\ln(k_p/k_{p=1}) = 1.004 \times 10^{-3} P - 2.5 \times 10^{-8} P^2, \tag{1}$$
$$R = 0.9966, \quad N = 7,$$

$$\ln(k_p/k_{p=1}) = 29.92 \ln\left[(30483 + P)/30483\right], \tag{2}$$
$$R = 0.9961, \quad N = 7.$$

Ratio (1) assumes a false peak at 20 kbar, while Eq. (2) can reliably predict the change in the reaction rate in the region of high pressures, which is important when planning applied work under pressure.

The experimental value of $\Delta V_{exp}^{\neq}$ at atmospheric pressure was determined using the relation:

$$[\partial \ln(k_p/k_{p=1})/\partial P]_{P=1} = -\Delta V_{exp}^{\neq}/RT. \tag{3}$$

The corrected value of the activation volume, $\Delta V_{corr}^{\neq}$, was found by considering the compression of the solvent under pressure [20]:

$$\Delta V_{corr}^{\neq} = \Delta V_{exp}^{\neq} + (n-1)\beta RT, \tag{4}$$

where n is the order of the reaction; β is the compressibility factor of acetonitrile, 1.13×10^{-4} bar^{-1} [27], R is the gas constant (83.14 cm^3 bar mol^{-1} K^{-1}); and $T = 298$ K. The corrected value, $\Delta V_{corr}^{\neq}$, is -22.0 ± 0.9 and -21.5 ± 1.1 cm^3 mol^{-1} from the ratios of (1) and (2),

respectively. Minimal values of the activation volumes are observed for the DARs with substituted anthracenes [17, 18, 28]. In the reactions between maleic anhydride and 9,10-dimethylanthracene and 9-phenylanthracene in toluene at 25°C, the $\Delta V_{corr}^{\neq}$ values are thus -19.7 ± 0.8 and -19.6 ± 0.7 cm^3 mol^{-1}, respectively [28].

CONCLUSIONS

The activity of substituted anthracenes in the reaction with maleic anhydride changes in the order 9,10-dimethylanthracene > 9,10-anthracenedimethanol > 9-methylanthracene > 9-anthracenemethanol. The effect solvents on the reaction rate of $1 + 2 \rightarrow 3$ is slight, and there is no activating effect of the formation of H-bond reagents in chloroform. For substituted anthracenes, the reaction rate depends strongly on the nature of the substituent, which is determined mainly by the difference between the activation enthalpies [29]. This is consistent with the conclusion that changes in the values of activation volume correlate better with changes in entropy than with changes in enthalpy of activation [30].

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