

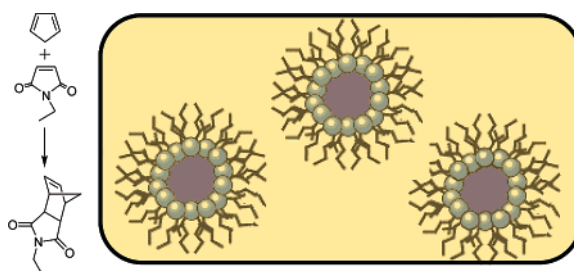
Water in Oil Microemulsions as Reaction Media for a Diels–Alder Reaction between *N*-Ethylmaleimide and Cyclopentadiene

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The Diels–Alder reaction between *N*-ethylmaleimide and cyclopentadiene in water/AOT/isooctane microemulsions, where AOT denotes sodium bis(2-ethylhexyl)sulfosuccinate, was studied. The rate of the reaction was found to be higher than that obtained in pure isooctane, irrespective of the particular microemulsion composition used. The efficiency of this catalytic action ranged from a factor of 3 at low water contents (viz., $W = [\text{H}_2\text{O}]/[\text{AOT}] = 2$) to 15 at $W = 35$. On the basis of these results, the reaction takes place simultaneously in the continuous medium and at the microemulsion interface. The favorable arrangement of the reactants at the interface results in more than 95% of the reaction occurring in this microenvironment. The kinetic analysis revealed the rate constant at the microemulsion interface to change with the water content. For small W values a bimolecular rate constant at the interface close to that observed in hexane was obtained. This value increases with W and for $W > 20$, a value close to that obtained in ethanol was found. This can be ascribed to the absence of hydrogen bonding at the microemulsion interface as well as the accelerating effects due to enforced hydrophobic interactions.

Introduction

Diels–Alder (DA) reactions provide a powerful synthetic tool in organic chemistry and constitute the key step in the preparation of a large number of six-membered rings.¹ Its selectivity and yield can be enhanced in a number of ways,² particularly in an aqueous medium.³ Thus, water increases the reaction rate with respect to the usual organic solvents, and it also results in larger endo/exo ratios. A number of attempts at accelerating DA reactions have been made by using ionic liquids

as reaction media, where a solvophobic effect similar to that occurring in an aqueous medium has been suggested.⁴ The use of Lewis acids in the aqueous medium has become the most widely used choice in this context in recent years.⁵ In fact, the joint use of Lewis acids and colloid aggregates, micelles, and vesicles has aroused much interest lately on account of their enormous accelerating effects on the reaction.^{1,6,7}

In this work, we studied the influence of microemulsions on the DA reaction. Microemulsions are pseudohomogeneous mixtures of an organic solvent, water, and surfactant. Their use as reaction media has the advantage that they constitute efficient solvents for both inorganic salts and nonpolar organic molecules

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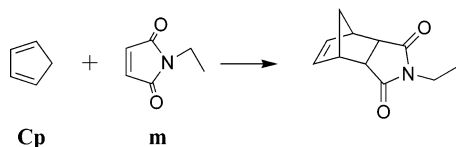
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SCHEME 1



and, hence, for reactions between compounds of rather different solubility.^{8,9} Because reactants may occupy separate compartments in them and the water that they contain exhibits special properties, microemulsions are being increasingly used as microreactors.¹⁰

In the present study, we examined the DA reaction between *N*-ethylmaleimide (m) and cyclopentadiene (Cp; Scheme 1), which has been widely studied in both aqueous and micellar media.¹¹ On the basis of the limited water solubility of cyclopentadiene, the reaction must largely take place both at the interface and in the continuous medium. Our results, however, suggest that the reaction in the continuous medium accounts for less than 10% of the overall process and that the interface of the AOT-based microemulsion is the main reaction zone.

Experimental Section

AOT was obtained from Aldrich and vacuum-dried in a desiccator for 2 days prior to use without further purification. *N*-Ethylmaleimide was purchased in the highest available purity from Fluka and used as received. Cyclopentadiene was obtained by distillation of bicyclopentadiene from Fluka immediately prior to use. The distillate was used to prepare solutions containing an approximate concentration of 0.8 M in isooctane from Aldrich.

Scheme 2 shows the composition of the water-in-oil microemulsions used, which spanned wide content ranges, namely, 5–35% w/w for AOT, 6–22% w/w for water, and 42–93% w/w isooctane. The corresponding *W* values ($W = [\text{H}_2\text{O}]/[\text{AOT}]$) ranged from 2 to 35.

The observed rate constants, k_{obs} , in the water/AOT/isooctane microemulsions were determined under pseudo-first-order conditions from spectroscopic data obtained with a Varian Cary 50 UV spectrophotometer (specifically, from the decrease in absorbance at 298 nm as the dienophile disappeared from the reaction medium at 25.0 ± 0.1 °C). An *N*-ethylmaleimide concentration, $[\text{m}] = 4.0 \times 10^{-4}$ M, which was much smaller than that of cyclopentadiene ($[\text{Cp}] = 6.13 \times 10^{-3}$, 1.23×10^{-2} , and 1.79×10^{-2} M), was used in all experiments. For comparison, we also determined the bimolecular rate constant for the reaction in pure isooctane and found it to be $k_0 = 2.80 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

Results

To account for potential evaporation losses of the solvents and cyclopentadiene and to minimize errors, the rate constant (k_{obs}) was determined for three different concentrations of cyclopentadiene (viz., 6.13×10^{-3} , 1.23×10^{-2} , and 1.79×10^{-2} M). Figure 1 illustrates the excellent linear relationship between k_{obs} and $[\text{Cp}]$ in AOT-based microemulsions of $W = 5$. The slopes of the lines were used to calculate the apparent

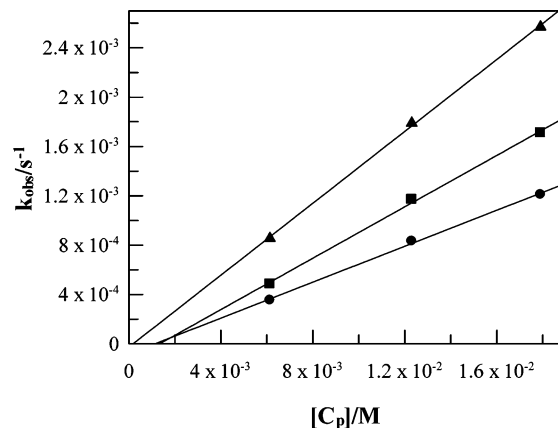


FIGURE 1. Influence of $[\text{Cp}]$ on k_{obs} for the DA reaction with *N*-ethylmaleimide. (●) $[\text{AOT}] = 0.103$ M, (■) $[\text{AOT}] = 0.206$ M, and (▲) $[\text{AOT}] = 0.514$ M; $W = 5$; $T = 25.0$ °C.

bimolecular rate constant, k_{app} , which is a function of the microemulsion composition:

$$k_{\text{obs}} = k_{\text{app}}[\text{Cp}] \quad (1)$$

Table 1 shows the k_{app} values obtained at variable surfactant concentrations and W values. As can be seen, there is a marked catalytic effect relative to the rate constant in pure isooctane ($k_0 = 2.80 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). The effect ranged from an increase in rate constant by a factor of 2 in microemulsions with a low water content ($W = 2$) to one of 15 for $W = 35$. The presence of this rate acceleration indicates that most of the reaction takes place in a more polar medium than that of isooctane (viz., the microemulsion interface). As will be shown below, on increasing the surfactant concentration and W , the amount of *N*-ethylmaleimide and cyclopentadiene incorporated to the interface becomes higher (see Figure 2 for *N*-ethylmaleimide distribution). On increasing the $[\text{AOT}]$ from 0.103 to 0.617, the percentage of *N*-ethylmaleimide at the interface increases typically from 5–10% to 75–95%, depending on the W value. This leads to an increase in the apparent rate constant upon going from $[\text{AOT}] = 0.103$ to $[\text{AOT}] = 0.617$ M, as can be seen from Table 1. On increasing W , we also increase the percentage of *N*-ethylmaleimide at the interface, resulting in an increase of the apparent rate constant with W . Moreover, the partitioning of cyclopentadiene along the microemulsion will be parallel to that of *N*-ethylmaleimide, increasing the apparent rate constant with increasing W and surfactant concentration.

Discussion

The kinetic data for reactions in water-in-oil microemulsions can only be interpreted in terms of reactivity if the local reactant concentrations and the intrinsic rate constants for the different pseudophases in the microemulsion can be obtained from apparent rate constants. Our group has developed a kinetic model based on the pseudophase formalism that can be used to obtain a quantitative interpretation of the influence of the microemulsion composition on chemical reactivity.¹² The pseudophase formalism was appropriate for the DA reaction between *N*-

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SCHEME 2. Microemulsion Compositions Used in the Present Study

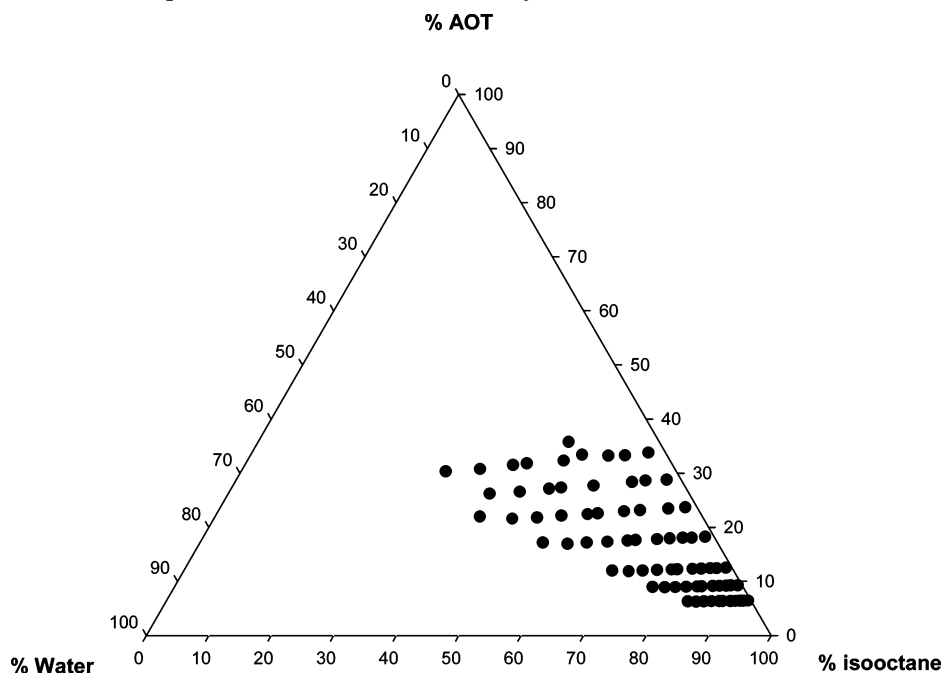


TABLE 1. Values for k_{app} for the DA Reaction of *N*-Ethylmaleimide with Cyclopentadiene in Water/AOT/Isooctane Microemulsions at 25.0 °C

[AOT]/M	$k_{app}/M^{-1} s^{-1}$									
	W = 2	W = 5	W = 7	W = 10	W = 13	W = 18	W = 20	W = 25	W = 30	W = 35
0.103	0.0594	0.0682	0.0912	0.0777	0.0975	0.1350	0.1130	0.1282	0.1473	0.1466
0.150	0.0690	0.0809	0.1113	0.0951	0.1208	0.1417	0.1455	0.1611	0.1792	0.1801
0.206	0.0727	0.0974	0.1241	0.1331	0.1473	0.1776	0.1825	0.1894	0.2059	0.2352
0.309	0.0830	0.1109	0.1564	0.1713	0.1823	0.2453	0.2253	0.2481	0.3076	0.2974
0.411	0.0932	0.1358		0.2000	0.2070	0.2618	0.2549	0.3085	0.4029	0.3822
0.514	0.1018	0.1458	0.1793	0.2219	0.2362	0.3800	0.3080	0.3838	0.4780	
0.617	0.0925	0.1258	0.2059	0.2553	0.2696	0.4537	0.3878	0.4085	0.5063	

ethylmaleimide and cyclopentadiene, assuming that the microemulsion consists of three different pseudophases: an aqueous phase (w), a medium essentially consisting of isooctane (o), and an interface consisting primarily of surfactant (i). On the basis of the solubility of our substrates in water and organic solvents, we assume cyclopentadiene to partition between the interface and the continuous medium and *N*-ethylmaleimide to be present in the three microemulsion pseudophases (Scheme 3).

For the application of the kinetic treatment, it is necessary that the partitioning reagent distribution along the microenvironments of the microemulsions is faster than the cycloaddition rate. The kinetics of solubilizate exchange between water droplets of a water-in-oil microemulsions have been widely studied by Robinson et al.,¹³ Fletcher et al.,¹⁴ and Pileni et al.¹⁵ Their approach involves an analysis of a reaction in a water-in-oil microemulsion involving reactant species totally confined within the dispersed water droplets, so that a necessary step prior to their chemical reaction is a transfer of reactants into the same droplet. When the chemical reaction is fast (close to

diffusion-controlled), the overall reaction rate is likely to be controlled by the rate of interdroplet transfer of reacting species. The interdroplet transfer rate was measured as a function of the droplet size, the temperature, the surfactant, and the continuous medium. Exchange rates were determined using very fast chemical reactions as indicators for exchange. Three types of reaction were investigated: proton transfer, metal–ligand complexation, and electron transfer. Similar exchange rates were found for all three reactions. For AOT as dispersant, exchange occurs with a second-order rate constant of 10^6 – 10^8 $M^{-1} s^{-1}$, depending on the droplet size and temperature. The exchange rate constants are 2–4 orders of magnitude slower than the droplet encounter rate, as predicted from simple diffusion theory.

The distribution of *N*-ethylmaleimide in the microemulsion can be characterized in terms of the partition constant between the aqueous phase and the interface, K_{wi}^m , and that between the continuous medium and the interface, K_{oi}^m . On the other hand, cyclopentadiene will only partition between isooctane and the interface, with K_{oi}^{Cp} . The expressions for the respective partition constants are as follows:

$$K_{wi}^m = \frac{[m]_i}{[m]_w} W \quad K_{oi}^m = \frac{[m]_i}{[m]_o} Z \quad K_{oi}^{Cp} = \frac{[Cp]_i}{[Cp]_o} Z \quad (2)$$

where Z , by analogy with W , is the isooctane-to-AOT concen-

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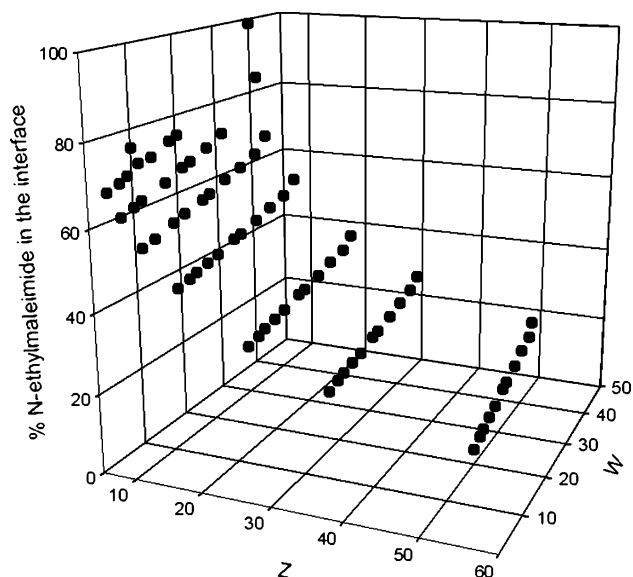
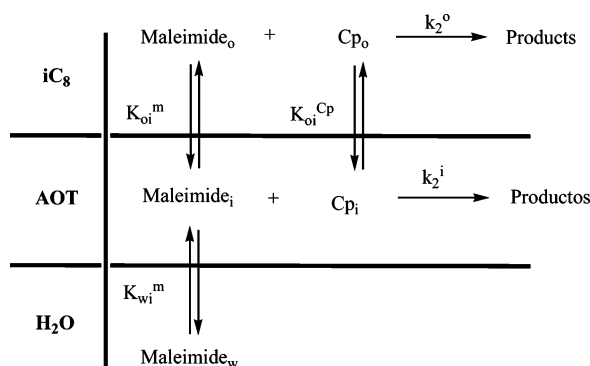


FIGURE 2. Variation of the proportion of *N*-ethylmaleimide at the interface as a function of the microemulsion composition parameters *Z* and *W*. Values of *Z* and *W* are simulated for clarity so they do not correspond to the experimental microemulsion compositions used in the kinetic study (see Scheme 2).

SCHEME 3. Reagent Distribution for the DA Reaction between *N*-Ethylmaleimide and Cyclopentadiene in AOT-Based Microemulsions



tration ratio; and $[m]_w$, $[m]_i$, and $[m]_o$ are the *N*-ethylmaleimide concentrations in the aqueous phase, interface, and continuous medium, respectively, all referred to the total microemulsion volume. The concentration of *N*-ethylmaleimide in each microemulsion pseudophase can be calculated on the assumption that the total concentration will be a combination of the three individual concentrations:

$$[m]_w = \frac{K_{oi}^m W [m]_T}{K_{oi}^m K_{wi}^m + K_{wi}^m Z + K_{oi}^m W} \quad (3)$$

$$[m]_i = \frac{K_{oi}^m K_{wi}^m [m]_T}{K_{oi}^m K_{wi}^m + K_{wi}^m Z + K_{oi}^m W} \quad (4)$$

$$[m]_o = \frac{Z K_{wi}^m [m]_T}{K_{oi}^m K_{wi}^m + K_{wi}^m Z + K_{oi}^m W} \quad (5)$$

The proportion of *N*-ethylmaleimide in each microenvironment was calculated by using partition constants determined in

previous work,¹⁶ namely, $K_{oi}^m = 16$ and $K_{wi}^m = 133$. As the parameter *W* varies, changes occur in the microviscosity of the microemulsion and the polarity. In this sense, the changes observed by various techniques¹⁷ are especially important when studying the properties of the solubilized water in AOT-based microemulsions. These changes in the physical properties of the water can modify the reactivity¹⁸ and even the mechanism by which the reactions occur.¹⁹ However, these effects are not reflected in the distribution constants of the reactants, K_{oi}^m and K_{wi}^m , because these remain independent of *W*. The reason for these different sensitivities must be found in the enthalpies of solvent transfer for ions and neutral molecules.²⁰

The proportions of *N*-ethylmaleimide in the water microdrops never exceeded 7%. Figure 2 shows the variation of the proportion of *N*-ethylmaleimide at the interface as a function of the microemulsion composition parameters *Z* and *W*. As can be seen, the proportion of this reactant at the interface increases with a decrease in *Z* at constant *W*. The increase is a result of drop size in those tests where their number was increasing with decreasing *Z*. Also, the proportion increased with increasing *W* (i.e., increasing number of drops) at constant *Z*. At a constant number of drops (i.e., constant *Z*), increasing their size (*W*) increased the interfacial volume and, hence, the proportion of *N*-ethylmaleimide that was incorporated into the interface. As can be seen in Figure 2, the proportion at the interface ranged from about 80% at small *Z* values to about 15% at large *Z* values. There was, therefore, a comparable proportion of *N*-ethylmaleimide in the continuous medium of the microemulsion available for reaction with cyclopentadiene.

On the basis of the way the reactants partition between the microemulsion pseudophases, the DA reaction can take place both at the interface and in the continuous medium. Therefore, its rate can be expressed as

$$\text{rate} = k'_i [m]_i + k'_o [m]_o \quad (6)$$

where k'_i and k'_o are the pseudo-first-order rate constants at the interface and in the continuous medium, respectively. To write the rate law as a function of the second-order rate constant, one must use the cyclopentadiene concentration at the interface as referred to the interface volume, $[Cp]_i^i$, and that in the continuous medium as referred to the oil volume, $[Cp]_o$:

$$\text{rate} = k_{\text{obs}} [m]_T = k_i [Cp]_i^i [m]_i + k_o [Cp]_o [m]_o \quad (7)$$

Equation 8 allows an expression of the reaction rate as a function of concentrations referred to the total microemulsion

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volume, namely, the concentration of Cp at the interface as referred to the total system volume, $[Cp]_i$, and that referred to the total microemulsion volume, $[Cp]_o$:

$$[Cp]_i = \frac{V_T}{V_{AOT}} [Cp]_i = \frac{1}{\bar{V}_{AOT}[AOT]} [Cp]_i [Cp]_o^0 = \frac{V_T}{\bar{V}_{iC_8}} [Cp]_o = \frac{1}{\bar{V}_{iC_8}[iC_8]} [Cp]_o$$

$$\text{rate} = k_i \frac{1}{\bar{V}_{AOT}[AOT]} [Cp]_i [m]_i + k_o \frac{1}{\bar{V}_{iC_8}[iC_8]} [Cp]_o [m]_o \quad (8)$$

Herein, \bar{V}_{AOT} and \bar{V}_{iC_8} are the molar volumes of the surfactant and the continuous medium, respectively.

Because of its low water solubility, cyclopentadiene will only partition between the continuous medium and the interface. This leads to the following equations for its concentration in the different microenvironments of the emulsion:

$$[Cp]_o = \frac{Z}{Z + K_{oi}^{Cp}} [Cp]_T \quad [Cp]_i = \frac{K_{oi}^{Cp}}{Z + K_{oi}^{Cp}} [Cp]_T \quad (9)$$

Substitution of eqs 3–5 and 9 into the rate law yields the following relation between the apparent rate constant and parameter Z :

$$k_{app} = \frac{1}{Z + K_{oi}^{Cp}} \frac{1}{(K_{oi}^m K_{wi}^m + K_{wi}^m Z + K_{oi}^m W)} \left\{ \frac{k_i K_{oi}^m K_{wi}^m K_{oi}^{Cp}}{\bar{V}_{AOT}[AOT]} + \frac{k_o K_{wi}^m Z}{\bar{V}_{iC_8}[AOT]} \right\} \quad (10)$$

Equation 10 can be rearranged as:

$$\frac{1}{k_{app} \bar{V}_{AOT} \bar{V}_{iC_8} [AOT] (K_{oi}^m K_{wi}^m + K_{wi}^m Z + K_{oi}^m W)} = \frac{K_{oi}^{Cp} + Z}{k_i K_{oi}^m K_{wi}^m K_{oi}^{Cp} \bar{V}_{iC_8} + k_o K_{wi}^m \bar{V}_{AOT} Z} \quad (11)$$

Because the partition constants for *N*-ethylmaleimide, $K_{oi}^m = 16$ and $K_{wi}^m = 133$, and the rate constant for its reaction with cyclopentadiene in isooctane, $k_o = 2.80 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, are known, the sole unknowns in eq 11 are the rate constant for the reaction at the interface, k_i , and the partition constant for cyclopentadiene, K_{oi}^{Cp} . Values for \bar{V}_{iC_8} and \bar{V}_{AOT} were taken as $\bar{V}_{iC_8} = 0.165 \text{ M}^{-1}$ and $\bar{V}_{AOT} = 0.37 \text{ M}^{-1}$. Under these considerations, eq 11 can be reduced to:

$$\frac{1}{k_{app}[AOT](2128 + 133Z + 16W)0.061} = \frac{K_{oi}^{Cp} + Z}{351k_i K_{oi}^{Cp} + 1.38Z} \quad (12)$$

As an example, Figure 3 shows the good fit of the experimental data to eq 12 for $W = 7, 20$, and 35 . From analogous fits to those shown in Figure 3, we can get the values for the partition constant of cyclopentadiene between the continuous medium and the interface of the microemulsion, K_{oi}^{Cp} , and for the DA

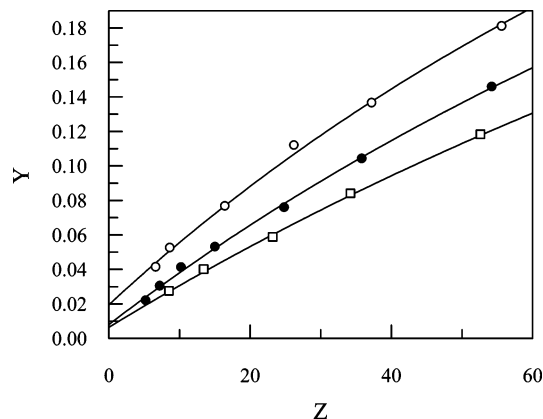


FIGURE 3. Fit of experimental data to eq 12 for (○) $W = 7$, (●) $W = 20$, and (□) $W = 35$. For simplicity, $Y = 1/k_{app}[AOT](2128 + 133Z + 16W)0.061$.

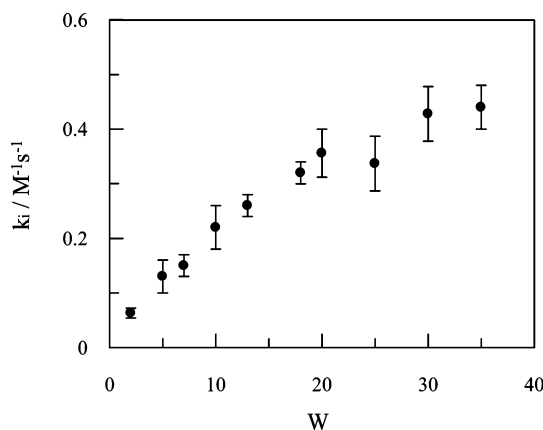


FIGURE 4. Bimolecular rate constant for the Diels–Alder reaction between cyclopentadiene and *N*-ethylmaleimide at the interface of AOT-based microemulsions at 25.0 °C.

rate constant at the interface, k_i . Table 2 shows the obtained values for K_{oi}^{Cp} at different W values. Only the de value for $W = 2$ deviates clearly from the mean value of $K_{oi}^{Cp} = 3.2$, calculated without considering $W = 2$.

From analogous fits, as those shown in Figure 3, the bimolecular rate constant for the DA reaction at the interface of the AOT-based microemulsion can be obtained. Figure 4 shows the k_i values for different water contents of the microemulsion. As can be seen, k_i values increase on increasing W , in accord with the increase of the polarity of the interface on increasing the water content of the microemulsion.

A comparison of the obtained k_i values with the rate constants for this reaction in organic solvents and in water (Table 3) reveals that the rate constants at the interface of water/AOT/isooctane microemulsions range between the value obtained in pure hexane and pure ethanol. For small water contents, $W = 2$, the bimolecular rate constant at the interface, $k_i = 0.063 \text{ M}^{-1} \text{ s}^{-1}$, is close to the value obtained in pure hexane, $k_o = 0.0529 \text{ M}^{-1} \text{ s}^{-1}$. On increasing the water content of the microemulsion, the rate constant at the interface also increases and for W values higher than 20, a bimolecular rate constant, $k_i = 0.44 \text{ M}^{-1} \text{ s}^{-1}$, is observed. This value is similar to that obtained in pure ethanol. In any case, the rate constant is at least 60 times smaller than that in bulk water. In this context, it is useful to consider the factors causing the strong acceleration of the reaction in the aqueous medium, namely, (a) hydrogen-bond stabilization of

TABLE 2. Values for K_{oi}^{Cp} Obtained by Using Eq 12 as a Function of W

W	2	5	7	10	13	18	20	25	30	35
K_{oi}^{Cp}	6 ± 2	4.0 ± 0.9	5.1 ± 0.8	2.4 ± 0.7	2.9 ± 0.2	3.2 ± 2.3	2.5 ± 0.4	3.1 ± 0.6	3 ± 1	2.5 ± 0.5

the activated complex^{11a,21} and (b) so-called “enforced hydrophobic interactions”.^{11a,22,23} The word “enforced” is used to stress the fact that hydrophobic interactions occur simply because they are an integral part of the activation process. When the reaction takes place at the interface of a microemulsion, virtually no hydrogen bonds are present at the interface and no rate acceleration due to enforced hydrophobic interactions is to be expected. Therefore, the DA reactions which take place at the microemulsion interface are slower than those in aqueous solution.

When comparing the bimolecular rate constants for the DA reaction between cyclopentadiene and *N*-ethylmaleimide in heptane and isooctane, we found no difference between the solvent polarity and the acceptor numbers of both solvents. However, the rate constant in hexane is approximately double that in isooctane, and the difference in reactivity can be correlated with the different internal pressures for both solvents: $P_{int} = 2326$ atm and $P_{int} = 2578$ atm for isooctane and hexane, respectively.²⁴ The cohesive energy density or the internal pressures have been successfully correlated with rate constants of some DA reactions.²⁵ Internal pressure is thought to reflect highly distance-dependent dispersion and dipole–dipole interactions within the solvent and was proposed to influence the rate in the same way external pressure does. However, because the internal pressure of water is very low, this effect cannot account for the accelerating effect of water.²⁴

As was pointed out previously, hydrogen-bond stabilization of the activated complex was proposed as a factor causing the strong acceleration of the DA reaction in aqueous medium. In fact, it was proposed that the rate of DA reactions increase on increasing the electrophilic character of the solvent. We can compare in Figure 5 the bimolecular rate constants at the interface of the microemulsion for the DA reaction of cyclopentadiene with *N*-ethylmaleimide (data from Figure 4) with the ionizing power (Y_{Cl}) of the interface of AOT-based microemulsions.²⁶ The ionizing power and nucleophilicity of the interface of AOT-based microemulsions are influenced by the water content of the system. When W decreases, so does the ionizing power, because the strong interaction between the SO_3^- anionic headgroup of the surfactant and the water molecules decreases the electrophilic character of water. On the other hand, the nucleophilicity of the interface increases on decreasing W because such interaction increases the electronic density on the oxygen atom of the water molecules. As we can observe in Figure 5, the variation of the physical properties of the interface of AOT-based microemulsions can be considered as the cause for the variation of the rate constants shown in Figure 5.

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TABLE 3. Rate Constant for the DA Reaction between *N*-Ethylmaleimide and Cyclopentadiene in Various Media

solvent	$k/M^{-1} s^{-1}$
isooctane	0.0280
hexane ^a	0.0529
interface of the AOT microemulsion	0.063–0.44
acetonitrile ^a	0.126
ethanol ^a	0.354
propanol ^a	0.411
TFE ^a	5.04
water ^a	21.6

^a From ref 11a.

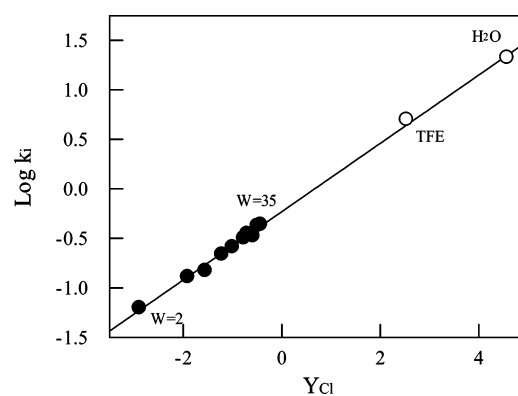


FIGURE 5. (●) Plot of $\log k_i$ for the DA reaction between cyclopentadiene and *N*-ethylmaleimide against Y_{Cl} at the interface of AOT-based microemulsions. (○) Values of $\log k$ for the reaction in TFE and water taken from ref 11a.

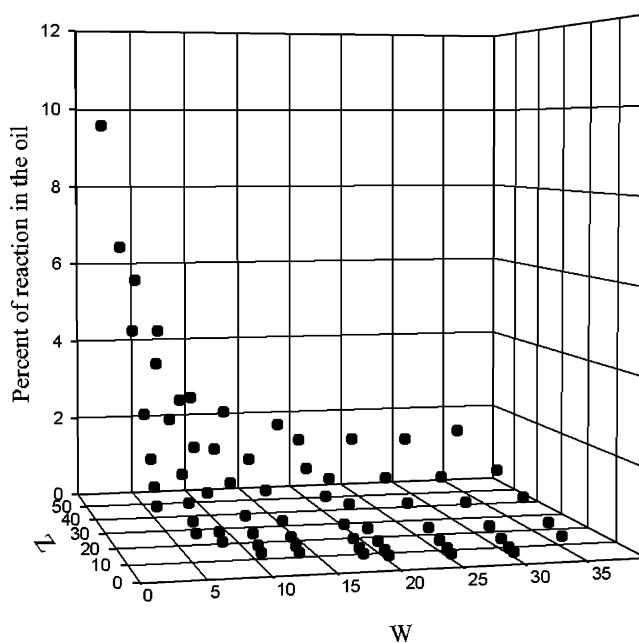


FIGURE 6. Proportion of the DA reaction between *N*-ethylmaleimide and cyclopentadiene occurring in the continuous medium of AOT-based microemulsions at 25.0 °C.

Figure 5 also shows the correlation between $\log k$ values for the DA reaction in water and TFE with the ionizing power of the solvent. These results fit the same correlation as those obtained at the interface of AOT-based microemulsions, showing that the solvent participation on the stabilization of the transition state by hydrogen bond is of major importance.

Our results allow the determination of the rate constant at the microemulsion interface as well as the rate constant for the DA reaction in pure isooctane. These two rate constants and the partition constants of *N*-ethylmaleimide and cyclopentadiene between the different microemulsion environments allow us to estimate to what extent the reaction is occurring in each phase. Figure 6 shows the percentage of the reaction in the continuous medium at variable Z and W values.

It should be noted that, except at $Z = 56.3$, the percentage of reaction in the continuous medium is always less than 5% and that it decreases with decreasing Z . This is consistent with the proportion of *N*-ethylmaleimide at the microemulsion interface increasing with decreasing Z (Figure 2) and the opposite effect for the proportion in the continuous medium. Also, the percentage of the reaction was slightly affected by the microemulsion composition via parameter W . Thus, the reaction in the continuous medium invariably decreases with increasing W , and the opposite is true of the proportion at the interface. This is

consistent with the proportion of *N*-ethylmaleimide at the interface increasing with an increase in drop size.

Conclusions

Water-in-oil microemulsions can be considered as an alternative reaction media for DA reactions, where solubility problems can be overcome. Depending on the hydrophobicity of the reagents and the microemulsion composition, the reaction takes place simultaneously in the continuous medium and the interface of the microemulsion. The different polarities of the microenvironments of the microemulsions are responsible for the reaction rate acceleration with respect to the continuous medium of the microemulsion. By using the pseudophase formalism, the DA rate constants in the interface of the microemulsion can be obtained for different water contents. Our results show that the rate constants at the interface increase from a value close to that observed in pure hexane to one close to that observed in ethanol on increasing the water content.

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