

# Chemical Reactions in Microemulsions: Kinetics of the Alkylation of 2-Alkylindan-1,3-diones in Microemulsions and Polar Organic Solvents

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The kinetics of the alkylation of 2-alkylindan-1,3-diones by benzyl bromide has been studied in microemulsions and polar organic solvents. In microemulsions the reaction proceeds at the microscopic water/oil interface. The solvent properties of this interfacial environment are assumed to be similar to those of methanol. In order to describe the kinetics of reactions occurring in microemulsions stabilized by non-ionic amphiphiles, the volume of the microemulsion is divided into three regions: water-rich, oil-rich and interfacial regions. The interfacial region is treated as a two-dimensional interface or as an interfacial volume.

Microemulsions have been proposed as solvents for chemical reactions in a number of publications.<sup>1-4</sup> They are good solvents for both non-polar organic molecules and polar inorganic salts and therefore appear to be excellent media for facilitating reactions between these different reactants. Microemulsions are thermodynamically stable colloidal dispersions of either water in oil or oil in water, stabilized by the addition of an amphiphile. The phase behaviour of such ternary mixtures of water, oil and a non-ionic amphiphile is well understood.<sup>5-7</sup> Investigations of the microstructure of microemulsions show that these systems are heterogeneous on a microscopic scale.<sup>8</sup> They consist of microscopic domains of water and oil separated by a monolayer of amphiphile molecules. Different reactants solubilized in the microemulsion may meet and react at this microscopic interface. Microemulsions contain large internal interfaces compared to heterogeneous media, and therefore high reaction rates may be expected.

The alkylation of a carbanion by an alkyl halide is an example of a reaction between polar and non-polar reactants. This reaction is a step frequently used for synthesizing carboxylic acids or alkyl ketones.<sup>9,10</sup> In the present paper, 2-alkylindan-1,3-diones are alkylated at the 2-position by benzyl bromide. The proton at the 2-position is acidic and can be abstracted by a weak base. The carbanions of indan-1,3-diones absorb light with an absorbance maximum at ca. 450 nm, so that the progress of the reaction may be followed spectrophotometrically.

Benzyl bromide is water-insoluble and is therefore located in the non-polar domains of the microemulsion. The reaction is performed in the presence of sodium hydroxide as base, and the 2-alkylindan-1,3-dione is transformed, by exchange with sodium hydroxide, to the carbanion which is transferred to the aqueous domains of the microemulsion or to the internal interface. Indan-1,3-diones with different alkyl substituents in the 2-position have been studied in order to vary the partitioning of the carbanions between the aqueous domains and the internal interface. The reaction was also studied in different organic solvents, in order to be able to discuss the results obtained in microemulsions.

## Experimental

All solvents were of analytical grade and supplied by Merck, except for Igepal CA-520, which was supplied by Aldrich. 2-Alkylindan-1,3-diones were kindly provided by Dr. D.

Kuck, University of Bielefeld.<sup>11</sup> Benzyl bromide was distilled before use.

2-Alkylindan-1,3-diones were dissolved in the different solvents at concentrations of ca.  $3 \times 10^{-4}$  mol dm<sup>-3</sup>, and sodium hydroxide was added to guarantee complete deprotonation of the indandiones. It was checked that the reaction rate was independent of the concentration of sodium hydroxide. The alkaline solutions of indan-1,3-dione were thermostatted at the temperature of the experiment. The measurements were started by injecting a small volume of benzyl bromide into the solution by using a microlitre syringe. After shaking the sample the recording of the absorbance of the solution was started. The absorbance maxima of the different substituted anions  $\text{RId}^-$  were as follows: 450 nm for R = methyl, 451 nm for R = ethyl, 449 nm for R = isopropyl and 445 nm for R = benzyl. In the presence of sodium hydroxide, the reaction of benzyl bromide to yield benzyl alcohol has been discussed as a possible side reaction.<sup>12</sup> However, in our study the concentration of NaOH was so small that this reaction could not be observed.

The solvents used as reaction media are methanol, ethanol, *N,N*-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and microemulsions ( $\mu\text{E}$ ) of different composition. The microemulsions are mixtures of water, heptane and the non-ionic amphiphile Igepal CA-520 [ $\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-(\text{O}-\text{CH}_2-\text{CH}_2)_5-\text{OH}$ ]. Their composition is given by  $\alpha = m_0/(m_0 + m_w)$  and  $\gamma = m_s/(m_s + m_0 + m_w)$ ;  $m_0$ ,  $m_w$  and  $m_s$  are mass of heptane, water and Igepal, respectively. Two sections of the phase prism of this ternary system are shown in Fig. 1. The phase behaviour follows the general pattern of systems with non-ionic amphiphiles as described in ref. 5. Six microemulsions of different composition were studied. The amphiphile concentration  $\gamma$  was varied at a constant ratio of water to heptane for  $\mu\text{E}$  1-3. At constant concentration of amphiphile of  $\gamma = 15\%$ ,  $\alpha$  was varied from 29 to 71% in order to change the system from a water-rich to an oil-rich microemulsion ( $\mu\text{E}$  1, 4 and 5). The composition of the microemulsions is given in Table 1. The experiments were performed at temperatures where the microemulsions (including benzylbromide) are stable one-phase systems.

## Results

In organic solvents a condensation reaction of the 2-alkylindan-1,3-diones is observed between the anion  $\text{RId}^-$  and indandione  $\text{RIdH}$ .<sup>13</sup> In order to prevent this side reac-

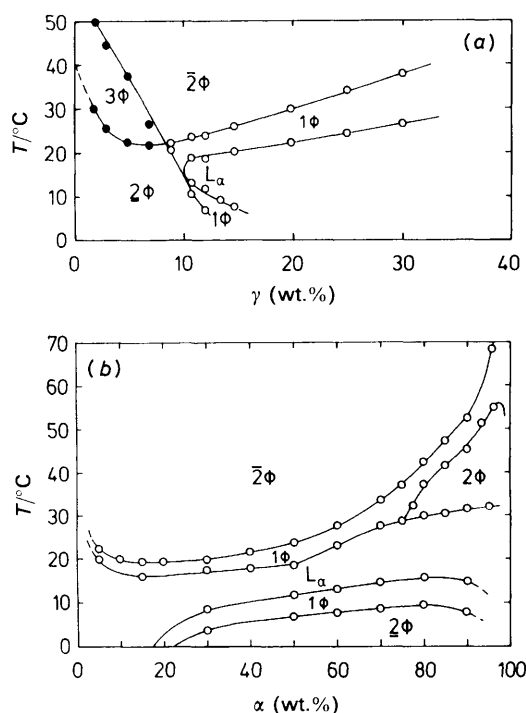
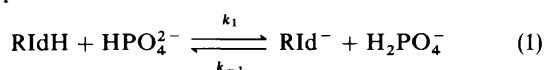


Fig. 1 Sections of the phase prism of ternary mixtures of water, heptane and Igepal CA 520 at constant ratio of heptane to water 1 : 1 ( $\alpha = 50$  wt.%) (a) and at constant amphiphile concentration  $\gamma = 12$  wt.% (b). 1 $\phi$ , 2 $\phi$  and 3 $\phi$  indicate one-, two- and three-phase regions, respectively.  $L_\alpha$  indicates a lamellar region

tion, complete dissociation of the indandiones has to be guaranteed, and therefore their dissociation constants were determined in aqueous solution.<sup>14</sup>

The dissociation of RIdH has to be studied in buffered solutions. With phosphate buffer the dissociation is connected with the proton-transfer reaction



The dissociation constants of RIH were determined both by photometric titration and by kinetic measurements, from which both rate constants and equilibrium constants  $K_a$

$$K_a(\text{RIH}) = \frac{k_1}{k_{-1}} \frac{1}{K_a(\text{H}_2\text{PO}_4^-)} \quad (2)$$

are obtained. Photometric and kinetic measurements yield the same  $pK_a$  values, and the results are summarized in Table 2. Since all  $pK_a$  values are close to 7 a small excess of sodium hydroxide is sufficient for complete dissociation of RIH. The reaction scheme, given in Fig. 2, is abbreviated as

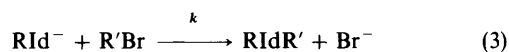


Table 1 Composition and temperature of the microemulsions studied

microemulsion	water (wt.%)	heptane (wt.%)	Igepal (wt.%)	$T/^\circ\text{C}$
$\mu\text{E } 1$	42.5	42.5	15	20
$\mu\text{E } 2$	40	40	20	25
$\mu\text{E } 3$	37.5	37.5	25	25
$\mu\text{E } 4$	60	25	15	26
$\mu\text{E } 5$	25	60	15	27
$\mu\text{E } 6^a$	5	85	10	15–40

<sup>a</sup> This system contains cyclohexane instead of n-heptane. It was chosen because of its large single-phase temperature interval.

Table 2  $pK_a$  values of 2-alkylindan-1,3-diones in aqueous solution at  $T = 25^\circ\text{C}$ , and absorption coefficients of RIdH and RId<sup>−</sup>

R	$pK_a$	$\lambda$ /nm	$\epsilon$ (RId <sup>−</sup> ) /dm <sup>3</sup> mol <sup>−1</sup> cm <sup>−1</sup>	$\epsilon$ (RIdH) /dm <sup>3</sup> mol <sup>−1</sup> cm <sup>−1</sup>
methyl	6.2	450	1930	70
ethyl	6.5	451	1950	80
isopropyl	7.4	449	1960	20
benzyl	5.9	445	1980	10

With a large excess of benzyl bromide  $[\text{R}'\text{Br}] \gg [\text{RId}^-]$ , the reaction is forced to follow pseudo-first-order kinetics

$$k_{\text{obs}} = 1/\tau = k[\text{R}'\text{Br}] \quad (4)$$

Since the absorbance of the solutions is given by

$$A = \epsilon l [\text{RId}^-] \quad (5)$$

an exponential decay of the absorbance

$$A = A_0 \exp(-t/\tau) \quad (6)$$

is observed. The time constants determined are in the range  $\tau = 20\text{--}10^4$  s.

Tables 3–6 summarize rate constants and activation parameters for the alkylation of the four 2-alkylindan-1,3-diones in different solvents. Each rate constant is determined from measurements at four to six concentrations of benzyl bromide. The activation energies are calculated from the rate constants determined at four to six temperatures. Temperature and concentration ranges are given in the tables. The activation energy,  $E_a$ , is determined from an Arrhenius plot, and the activation entropy is calculated according to the equation

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln k + R \ln \frac{h}{k_B T} \quad (7)$$

with  $\Delta H^\ddagger = E_a - RT$ .  $h$  is Planck's constant and  $k_B$  is the Boltzmann constant. The errors of the data given in the tables are as follows:  $\pm 10\%$  for  $k$ ,  $\pm 5$  kJ mol<sup>−1</sup> for  $E_a$  and  $\pm 20$  J mol<sup>−1</sup> K<sup>−1</sup> for  $\Delta S^\ddagger$ . The rate constant of the reaction in microemulsions had to be measured at the temperature required for a stable one-phase system. For a comparison of the different data, the corresponding rate constants at  $20^\circ\text{C}$  have been calculated using an activation energy of 58 kJ mol<sup>−1</sup> determined for  $\mu\text{E } 2$  and  $\mu\text{E } 6$ .

## Discussion

Table 7 summarizes the rate constants of the alkylation and the relative permittivities<sup>15</sup> of the solvents. For a given solvent very similar rate constants are determined for the alkylation of 2-methyl- and 2-ethylindan-1,3-dione. For 2-isopropyl- and 2-benzylindan-1,3-dione smaller rate constants are observed, as expected from Taft's  $E_s$  parameters for the different substituents. The activation parameters show no significant variation for the different solvents. This means that for all systems studied the reaction follows the same mechanism.

Changing the solvent from methanol ( $\epsilon_r = 32.6$ ) to ethanol ( $\epsilon_r = 24.3$ ) causes no significant change of the rate constants. On the other hand, for methanol ( $\epsilon_r = 32.6$ ) and acetonitrile

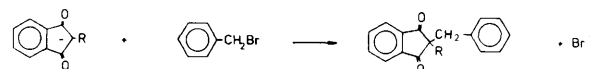


Fig. 2 Reaction scheme of the alkylation of 2-alkylindan-1,3-diones by benzyl bromide

**Table 3** Rate constants and activation parameters of the alkylation of 2-methylindan-1,3-dione with benzyl bromide at  $T = 20^\circ\text{C}$ 

solvent	$k$ / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$E_a$ / $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ / $\text{J mol}^{-1} \text{K}^{-1}$	$[\text{R}'\text{Br}]$ / $\text{mol dm}^{-3}$	$T/^\circ\text{C}$
methanol	$2.6 \times 10^{-3}$	69	-70	0.40-0.84	14-35
ethanol	$3.2 \times 10^{-3}$	64	-80	0.40-0.84	20-40
acetonitrile	$1.4 \times 10^{-1}$	48	-110	0.014-0.40	15-35
DMF	$1.7 \times 10^{-1}$	47	-110	0.007-0.140	15-35
DMSO	$3.2 \times 10^{-1}$	69	-30	0.014-0.140	19-40
$\mu\text{E } 1$	$6.2 \times 10^{-3}$	—	—	0.056-0.083	20

$[\text{R}'\text{Br}]$  and  $T$  indicate the concentration and temperature intervals of the experiments.

**Table 4** Rate constants and activation parameters of the alkylation of 2-ethylindan-1,3-dione with benzyl bromide at  $T = 20^\circ\text{C}$ 

solvent	$k$ / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$E_a$ / $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ / $\text{J mol}^{-1} \text{K}^{-1}$	$[\text{R}'\text{Br}]$ / $\text{mol dm}^{-3}$	$T/^\circ\text{C}$
methanol	$2.6 \times 10^{-3}$	66	-80	0.53-0.84	20-40
ethanol	$3.2 \times 10^{-3}$	65	-80	0.53-0.84	20-35
acetonitrile	$1.0 \times 10^{-1}$	55	-80	0.014-0.056	20-35
DMF	$1.4 \times 10^{-1}$	56	-80	0.014-0.056	20-35
DMSO	$3.7 \times 10^{-1}$	62	-50	0.014-0.140	19-40
$\mu\text{E } 1$	$6.7 \times 10^{-3}$	—	—	0.058-0.083	20

**Table 5** Rate constants and activation parameters of the alkylation of 2-isopropylindan-1,3-dione with benzyl bromide at  $T = 20^\circ\text{C}$ 

solvent	$k$ / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$E_a$ / $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ / $\text{J mol}^{-1} \text{K}^{-1}$	$[\text{R}'\text{Br}]$ / $\text{mol dm}^{-3}$	$T/^\circ\text{C}$
methanol	$5.8 \times 10^{-4}$	60	-110	0.06-0.76	10-45
ethanol	$1.4 \times 10^{-3}$	59	-110	0.32-0.76	10-40
acetonitrile	$4.8 \times 10^{-2}$	57	-80	0.05-0.12	10-35
DMF	$3.0 \times 10^{-2}$	50	-110	0.05-0.12	10-45
DMSO	$5.0 \times 10^{-2}$	51	-100	0.003-0.017	20-50
$\mu\text{E } 1$	$2.2 \times 10^{-3}$	—	—	0.024-0.083	20

**Table 6** Rate constants and activation parameters of the alkylation of 2-benzylindan-1,3-dione with benzyl bromide at  $T = 20^\circ\text{C}$ 

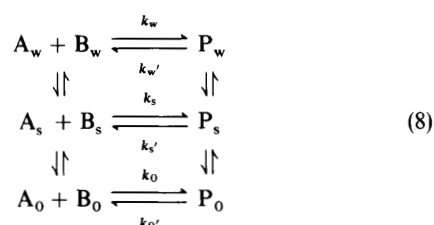
solvent	$k$ / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$E_a$ / $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ / $\text{J mol}^{-1} \text{K}^{-1}$	$[\text{R}'\text{Br}]$ / $\text{mol dm}^{-3}$	$T/^\circ\text{C}$
methanol	$1.6 \times 10^{-3}$	69	-60	0.25-0.70	15-40
ethanol	$1.3 \times 10^{-3}$	65	-90	0.25-0.76	25-45
acetonitrile	$9.2 \times 10^{-2}$	48	-110	0.017-0.085	25-45
DMF	$7.6 \times 10^{-2}$	56	-90	0.017-0.051	15-35
DMSO	$1.8 \times 10^{-1}$	67	-40	0.017-0.051	20-35
$\mu\text{E } 1$	$6.4 \times 10^{-3}$	—	—	0.014-0.083	20
$\mu\text{E } 2$	$6.4 \times 10^{-3}$	58	-40	0.014-0.083	20-25
$\mu\text{E } 3$	$7.0 \times 10^{-3}$	—	—	0.014-0.083	25
$\mu\text{E } 4$	$9.5 \times 10^{-3}$	—	—	0.014-0.083	26
$\mu\text{E } 5$	$6.3 \times 10^{-3}$	—	—	0.014-0.083	27
$\mu\text{E } 6$	$2.9 \times 10^{-3}$	58	-100	0.014-0.083	15-30

**Table 7** Rate constants ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) of the alkylation of substituted indandiones **RIH** with benzyl bromide in organic solvents and a microemulsion at  $T = 20^\circ\text{C}$ ; the values in brackets give the relative permittivity of the solvents<sup>14</sup>

solvent ( $\epsilon_r$ )	R			
	methyl	ethyl	isopropyl	benzyl
methanol (32.6)	$2.6 \times 10^{-3}$	$2.6 \times 10^{-3}$	$5.8 \times 10^{-4}$	$1.6 \times 10^{-3}$
ethanol (24.3)	$3.2 \times 10^{-3}$	$3.2 \times 10^{-3}$	$1.4 \times 10^{-3}$	$1.3 \times 10^{-3}$
acetonitrile (37.5)	$1.4 \times 10^{-1}$	$1.0 \times 10^{-1}$	$4.8 \times 10^{-2}$	$9.2 \times 10^{-2}$
DMF (37.7)	$1.7 \times 10^{-1}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-2}$	$7.6 \times 10^{-2}$
DMSO (45.0)	$3.2 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.0 \times 10^{-2}$	$1.8 \times 10^{-1}$
$\mu\text{E } 1$	$6.2 \times 10^{-3}$	$6.7 \times 10^{-3}$	$2.2 \times 10^{-3}$	$6.4 \times 10^{-3}$

( $\epsilon_r = 37.5$ ), i.e. two solvents of similar relative permittivity, the rate constants differ by more than an order of magnitude. This means there is no correlation between the rate constant and the relative permittivity of the solvent, and an  $S_N1$  mechanism can be excluded, since for this mechanism the rate constants increase with increasing relative permittivity.<sup>16</sup> A pronounced difference can be seen between the polar protic solvents (ethanol and methanol) and the polar aprotic solvents (DMF, DMSO and acetonitrile). This behaviour is typical for reactions following an  $S_N2$  mechanism.

Having determined the mechanism of the reaction in homogeneous solvents, now its kinetics in microemulsions will be discussed. Several models have been developed to describe the kinetics of reactions in microheterogeneous media, which are mainly based on the work of Berezin *et al.*<sup>17</sup> Models for reactions in aqueous micellar solutions divide these systems into three pseudophases: the micellar core, a charged surface gathering the ionic reactants of opposite charge, and the bulk water.<sup>18,19</sup> The distribution of the reactants between the pseudophases is diffusion controlled and therefore fast compared to the chemical reaction studied. For microemulsions we also consider a model dividing the volume into three subvolumes, the oil-rich domains ( $V_o$ ), the water-rich domains ( $V_w$ ) and an interfacial volume ( $V_s$ ). The reaction  $A + B \rightleftharpoons P$  may occur in all three subvolumes and is described by the following reaction scheme



The indices refer to the domains in which the molecules or ions are dissolved. The overall amount of a molecule or ion distributed over the three pseudophases is given by (here for A)

$$n_A = n_A^w + n_A^o + n_A^s = c_A^w V_w + c_A^o V_o + c_A^s V_s \quad (9)$$

$c_A^i$  is the concentration of A in region  $i$ . For the reaction occurring simultaneously in all three pseudophases the rate law is

$$\begin{aligned}
 -\frac{dn_A}{dt} = & V_w k_w c_A^w c_B^w + V_s k_s c_A^s c_B^s + V_o k_o c_A^o c_B^o \\
 & - V_w k_{w'} c_P^w - V_s k_{s'} c_P^s - V_o k_{o'} c_P^o
 \end{aligned} \quad (10)$$

Under pseudo-first-order conditions, i.e.  $c_B \gg c_A$ , an exponential decay of the concentration of A is observed. The time constant of this decay is given by:

$$\begin{aligned}
 \frac{1}{\tau} = & \frac{k_w c_B \phi_w}{\phi_w + P_A \phi_s + Q_A \phi_o} \frac{1}{\phi_w + P_B \phi_s + Q_B \phi_o} \\
 & + \frac{k_s c_B \phi_s P_A P_B}{\phi_w + P_A \phi_s + Q_A \phi_o} \frac{1}{\phi_w + P_B \phi_s + Q_B \phi_o} \\
 & + \frac{k_o c_B \phi_o Q_A Q_B}{\phi_w + P_A \phi_s + Q_A \phi_o} \frac{1}{\phi_w + P_B \phi_s + Q_B \phi_o} \\
 & + \frac{k_{w'} \phi_w}{\phi_w + P_P \phi_s + Q_P \phi_o} + \frac{k_{s'} \phi_s P_P}{\phi_w + P_P \phi_s + Q_P \phi_o} \\
 & + \frac{k_{o'} \phi_o Q_P}{\phi_w + P_P \phi_s + Q_P \phi_o}
 \end{aligned} \quad (11)$$

with the volume fractions  $\phi_i = V_i/V$ , the overall concentration  $c_B = n_B/V$ , and the partition coefficients

$$P_X = \frac{c_X^s}{c_X^w} \quad (12)$$

and

$$Q_X = \frac{c_X^o}{c_X^w} \quad (13)$$

Analogously a two-phase model may be considered, where a non-polar subvolume  $V_o$  and an aqueous subvolume  $V_w$  are separated by a two-dimensional interface of the area  $F$ . The concentrations of the reactants at this interface are expressed as surface concentrations  $\Gamma_A = n_A^s/F$ . The time constant is derived for the reaction performed under pseudo-first-order conditions, replacing  $c_A^s V_s$  by  $\Gamma_A F$  in eqn. (9)

$$\begin{aligned}
 \frac{1}{\tau} = & \frac{k_w c_B \phi_w}{\phi_w + D_A \Theta + Q_A \phi_o} \frac{1}{\phi_w + D_B \Theta + Q_B \phi_o} \\
 & + \frac{k_s c_B \phi_s D_A D_B}{\phi_w + D_A \Theta + Q_A \phi_o} \frac{1}{\phi_w + D_B \Theta + Q_B \phi_o} \\
 & + \frac{k_o c_B \phi_o Q_A Q_B}{\phi_w + D_A \Theta + Q_A \phi_o} \frac{1}{\phi_w + D_B \Theta + Q_B \phi_o} \\
 & + \frac{k_{w'} \phi_w}{\phi_w + D_P \Theta + Q_P \phi_o} + \frac{k_{s'} \Theta D_P}{\phi_w + D_P \Theta + Q_P \phi_o} \\
 & + \frac{k_{o'} \phi_o Q_P}{\phi_w + D_P \Theta + Q_P \phi_o}
 \end{aligned} \quad (14)$$

with

$$D_X = \frac{\Gamma_X}{c_X^w} \quad (15)$$

and

$$\Theta = \frac{F}{V} \quad (16)$$

Both equations are equivalent with respect to the dependence of the time constant on the overall concentration of B and the partition coefficients of the molecules and ions between the different regions. There is no difference in treating the interface two-dimensionally or as interfacial volume.

For the reaction studied here, eqn. (11) can be simplified. It may be assumed that (i) benzyl bromide is very hydrophobic and therefore dissolves only in the oil and at the interface, i.e.

$$Q_B = \frac{c_B^o}{c_B^w} \gg 1 \quad (17)$$

(ii) the carbanions are dissolved only in the water or at the interface, i.e.

$$Q_A = \frac{c_A^o}{c_A^w} \ll 1 \quad (18)$$

(iii) the alkylation reaction is irreversible.

According to the limitations (i) and (ii), A and B meet only in the interfacial region and eqn. (11) is reduced to

$$\frac{1}{\tau} = k_s c_B \frac{P_B}{Q_B} \frac{1}{1 + \phi_w/(P_A \phi_s)} \frac{1}{\phi_o} \quad (19)$$

The ratio  $P_B/Q_B = c_B^s/c_B^o$  is the partition coefficient of B (in our experiments benzyl bromide) between the non-polar region and the interfacial region.

The alkylation of 2-benzylindan-1,3-dione by benzyl bromide is studied in microemulsions of different composi-



**Table 8** Rate constants of the alkylation reaction of benzylindandione at  $T = 20^\circ\text{C}$ , volume fractions of water, heptane and Igepal in microemulsions of different compositions and theoretically calculated values for  $X = k_s(c_B^s/c_B^0)/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for two partition coefficients  $P_A$ 

$\mu\text{E}$	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\phi_w$	$\phi_o$	$\phi_s$	$X (P_A = 5)$	$X (P_A = 10)$
$\mu\text{E } 1$	$6.4 \times 10^{-3}$	0.356	0.524	0.120	$5.6 \times 10^{-3}$	$4.5 \times 10^{-3}$
$\mu\text{E } 2$	$6.4 \times 10^{-3}$	0.339	0.499	0.162	$4.5 \times 10^{-3}$	$3.8 \times 10^{-3}$
$\mu\text{E } 3$	$7.0 \times 10^{-3}$	0.322	0.473	0.205	$4.3 \times 10^{-3}$	$3.8 \times 10^{-3}$
$\mu\text{E } 4$	$9.5 \times 10^{-3}$	0.544	0.327	0.129	$5.7 \times 10^{-3}$	$4.4 \times 10^{-3}$
$\mu\text{E } 5$	$6.3 \times 10^{-3}$	0.193	0.695	0.112	$5.9 \times 10^{-3}$	$5.1 \times 10^{-3}$

tion, see Table 1. The rate constants given in Table 6 are calculated using eqn. (4) and the experimentally determined values of  $\tau$ . For these calculations the microemulsion is treated as a homogeneous system and its microstructure is taken into account in eqn. (19). The comparison between eqn. (4) and (19) shows how the rate constant depends on the distribution of the reactants in the heterogeneous reaction medium:

$$k = k_s \frac{P_B}{Q_B} \frac{1}{1 + \phi_w/P_A \phi_s} \frac{1}{\phi_o} \quad (20)$$

For microemulsions consisting of the same components, the partition coefficients are assumed to be independent of the composition. Therefore, according to eqn. (20)

$$X = k\phi_o \left( 1 + \frac{\phi_w}{P_A \phi_s} \right) \quad (21)$$

should be constant for these microemulsions.

$X$  is estimated with the simplifications that the volume fractions of the pseudo-phases ( $V_o$ ,  $V_w$ ,  $V_o$ ) are taken to be equal to the volume fractions of the components. Benzylindandione is accumulated in the interfacial region owing to its amphiphilicity. Its partition coefficient  $P_A$  is not known, therefore in Table 8  $X$  is calculated with estimated values of  $P_A$ .

The composition of the microemulsions was varied over a wide range. Nevertheless the experimental values of  $k$  obtained are approximately constant with the exception of that for the water-rich  $\mu\text{E } 4$ . Therefore  $P_A$  can be estimated only from this value. With  $P_A = 10$ ,  $X$  is constant for all systems studied (see Table 8), as required by the theory.

Finally from eqn. (21) with the value calculated for  $X$  the fraction  $P_B/Q_B = c_B^s/c_B^0$  may be estimated in the following way. The reaction proceeds exclusively in the interfacial region, which is a protic environment.<sup>20</sup> In protic solvents the rate constant is *ca.*  $1.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (Table 7). Inserting this value and  $X = 4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  into eqn. (20) yields  $P_B/Q_B = 3$ . Although the error in the numerical values of  $P_A$  and  $P_B/Q_B$  will be relatively high, the treatment of the data shows that the reaction mechanism of the alkylation of benzylindandione is correctly described by the scheme in eqn. (8). The composition of the microemulsions has to be varied over a wider range in order to obtain more

accurate values for the partition coefficients and to develop a more detailed mechanism for the reaction in microemulsions.

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