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Phase Transfer Catalysis

1. A Contribution to the Investigation of the Reaction Between Phenol and Butyl Bromide

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Summary

Some basic types of phase transfer catalysts (PTC) were tested using the alkylation of phenol with butyl bromide as an example. Their activity decreases in the series ammonium salts - polyethylene-glycols - crown ethers. The reaction course is favourably affected by the polar solvent (dichloroethane), or by the nonpolar solvent (toluene) in the case of polyethyleneglycol. Immobilized catalytically active groups on the crosslinked polymer are always less active. The reaction rate in KOH is higher than in NaOH. The distribution of reaction components between the particular phases was investigated in detail, and conclusions regarding the reaction mechanism and kinetics were drawn from the distribution of concentrations.

Introduction

In the past, preparation of organic compounds by using salts in a water-organic medium met with problems due to the low rate of the reaction. Such a reaction is, e.g., the reaction between alkyl halides and phenoxides; the problem of the low reaction rate can be solved by using phase transfer catalysis. Regen studied this reaction as early as in 1977 with a strongly basic anion exchanger based on the styrene-divinylbenzene copolymer (PST) as the catalyst, PST-$CH_2N^+(CH_3)_2(n\text{-}C_4H_9)Cl^-$ (2% DVB, 12% ring substitution) and obtained a 97% conversion after 10 h at 90°C. The reaction was somewhat slower if PST-$CH_2O(CH_2CH_2O)_nCH_3$ was the catalyst; after 12 h at 110°,the conversion was 60% (REGEN et al. 1977). The polymer is a common phase for both systems and plays the role of a co-solvent for the water-organic medium. It may also raise the concentration of components in its microsurroundings and increase the stability of the transient reaction state (REGEN 1979a, REGEN et al. 1979b).

McKENZIE and SHERINGTON 1978 studied the reaction of phenoxides, and in particular, of potassium phenoxide with butyl bromide in toluene and found that in the presence of immobilized polyethyleneglycols the polymer with lower substitution is more active and the catalytic effect increases with the chain length. The initial reaction rates show that linear polymers which can form hydrogen bonds possess low activity (KELLY et al. 1979). The highest catalytic effect was observed with copolymers of polyethyleneglycol and styrene. An attempt to prove the mechanism of catalysis with crosslinked vinylpyridinium copolymers by using the thermodynamic factor and kinetic selectivity was unsuccessful. Although the latter factor is more likely, the reactivity was unexpectedly higher with 2-naphthoxide than with phenoxide. Differences in the sizes of both anions are not large, and their effect is superimposed by the higher value of the +I effect of the first anion (McKENZIE and SHERINGTON 1981).

The effect of the polymer and of the type of the solvent on a similar reaction was studied by AKABORI et al. 1978 who found that benzo-18-crown-6 bound on the polymer supports rather the O-alkylation than the C-alkylation; the reaction conditions suggest that the conversion of alkylation of phenoxide with allyl chloride decreases in the order of solvents:

$$H_2O > Et_2O > EtOH > C_6H_5OH > C_6H_6$$

The reaction between butyl chloride and potassium phenoxide in the presence of dibenzo-18-crown-6 crosslinked with formaldehyde was completed by BLASIUS et al. 1982 at 110°C within one hour with a 93% conversion.

Since up to now the basic causes of the effect of catalysts in the heterogeneous reaction between phenoxide and butyl bromide have not been proved and the individual types of catalysts have not been compared, these problems were studied in some detail.

Experimental Part

Investigation of the reaction kinetics

Into a reactor, 5 ml in volume, 2 mmols of phenol or sodium phenoxide (prepared by azeotropic dehydration), 0.312 mmols of PTC, 2 ml of 2.5 mol/l NaOH (or KOH) or 2 ml of distilled water and 2 ml of a mixture of dichloroethane or toluene with n-butyl bromide (volume ratio = 6:1 c_o = 0.3491 g = = 2.548 mmol of n-butyl bromide) were introduced with stirring. The reactor was thermostated to 50°C ± 0.03°C and stirred with a propeller stirrer (1300 r.p.m.) . Samples of the organic phase were taken from the reaction mixture and immediately analyzed on a gas chromatograph with a column 1 m long packed with Chromosorb N-AW-DMCS 0.16-0.20 mm with 10 wt.% PEG 1550 (mol.wt. 1300-1600) at 90°C. The actual concentrations of n-butyl bromide were calculated from two measurements performed on samples and calibration standards.

Assuming that the reaction was of pseudo-first order, the rate constants k_1 were calculated from the initial reaction rate r_1 :

$$k_1 = \frac{r_1}{c_o} \quad [s^{-1}]$$

The distribution of alkalimetal ions and of n-butyl bromide in the phases was studied in the same ratios of reaction components as the reaction, with the difference that the amounts used were 1 ml of the aqueous and 1 ml of the organic phase, and 0.15 g of tetra(n-butyl ammonium) bromide (TBAB). After stirring for 30 min at 50°C, 10 samples in an amount 0.2 ml each were taken from the lower part of the reactor and titrated with 0.1 mol/l HCl after the addition of 20 ml methanol-water mixture. The content of phenol and alkalis was determined from the titration curve.

Chemicals

Dowex 11, Dow Chemical Co., Midland, Michigan U.S.A. Capacity 4.0 mmol/g or 1.5 mmol/ml, particle size 1 mm, Cl^- form.- Amberlyst A 26, Rohm and Haas Co., Philadelphia, Pennsylvania U.S.A. Capacity 4.5 mmol/g or 1.1 mmol/ml, particle size 0.3-1.2 mm, Cl^- form.- Macroporous strongly basic anion exchanger with trimethyl ammonium groups.- G-Gel-60-PEG-600: Macroporous copolymer glycidylmethacrylate - ethylenedimethacrylate with immobilized polyethyleneglycol PEG 600 (0.76 mmol/g).[*] -DB-18-C-6 was prepared by employing the usual procedure according to PEDERSEN 1967.- DB-18-C-6 was crosslinked with formaldehyde by employing a procedure after BLASIUS et al.1982. The sorption capacity for NaOH: 1.1 mmol/g, particle size 0.050 - 0.1 mm. -If not stated otherwise, all the other chemicals used were reagent grade purity.

Results and Discussion

Distribution of reacting compounds in the phases was investigated for phenol, sodium hydroxide and butyl bromide. According to gas chromatographic data, the concentration of n-butyl bromide in the aqueous phase is below 0.009 mmol/l. The reaction can therefore occur only in the organic phase, into which NaOH or PhONa are transferred due to PTC. In spite of the rather rough interval, the distributions thus determined (Fig.1) indicate an increase in alkalinity in the organic phase (from 0.009 to 0.140 mmol/ml) caused by PTC, both in dichloroethane and in toluene. The phenol content always decreases in the aqueous phase towards the boundary layer. In the organic

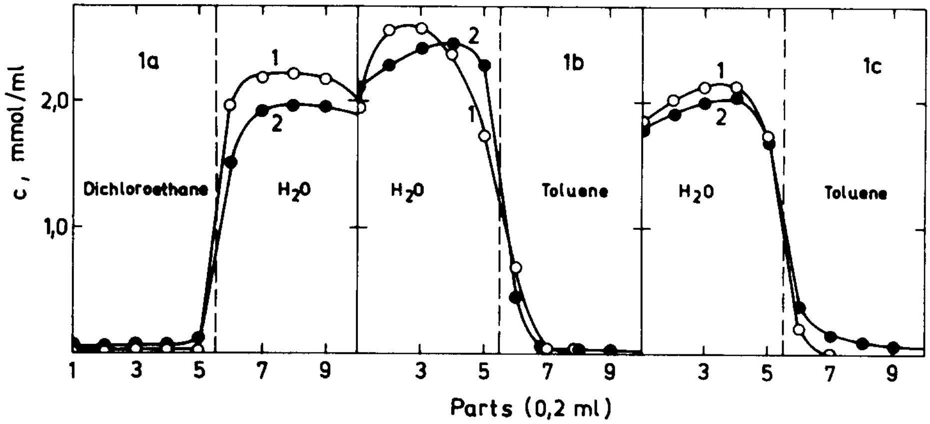

Fig.1 Distribution of reacting compounds in the water-organic phase:
1a System dichloroethane - 2.5 mol/l NaOH, 1b System toluene - 2.5 mol/l NaOH, 1c System toluene - 2.5 mol/l KOH; Curves: 1 without catalyst, 2 with catalyst TBAB

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[*] We are indebted to Dr.J.Kahovec who kindly supplied the sample.

phase it cannot be determined titrimetrically if present in low concentrations. The spectral determination (UV at 270 nm) is subjected to interference by products which due to their insolubility in water are present in the organic phase only (after 30 min 50% of the total amount of phenol). Without PTC, the concentration of alkali in the organic phase equals almost zero. The distribution of reactions of reacting compounds determined in this study show that the reaction takes place at the phase boundary.

Reaction kinetics. It can be said, on the basis of the distribution of concentrations of reacting compounds in both phases, that the concentration of phenoxide and alkali in the organic phase is controlled by PTC and is very low and constant until the compounds are consumed in the system.

Generally, the reaction may be assumed to be second-order both in the organic and in the aqueous phase. The resulting reaction rate is the sum of the reaction rates in the two phases:

$$r = k_o \, c_{PhOX_o} c_{BuBr_o} + k_v \, c_{PhOX_w} c_{BuBr_w}$$

where r is the reaction rate, k is the rate constant, c_{BuBr} and c_{PhOX} respectively are the concentrations of n-bromobutane and phenoxide, the subscripts o and w respectively denote the parameters of the organic and aqueous phases.

By substituting the initial concentrations of reacting compounds according to their solubility (Fig.1a) into the relation, it can be seen that in absence of the catalyst the initial reaction rate in both phases is restricted by the low concentration of reacting compounds, and that it is the same in both phases:

$$r_1 = 0.0025 \, k_o + 0.0070 \, k_w$$

In the case of PTC, the overall initial reaction rate increases due to the rise in alkalinity in the organic phase which is much higher than in absence of PTC:

$$r_2 = 0.1196 \, k_o + 0.005 \, k_w$$

These results allow us to neglect the contribution of the reaction rate in the aqueous phase. The relation then reads:

$$r_2 = k_o \, c_{PhPX_o} c_{BuBr_o}$$

and, as the concentration of phenoxide c_{PhOX} in the organic phase is much lower than in the aqueous phase, the concentration of this compound in the organic phase is constant until both concentrations of phenoxide in the two phases coincide. The reaction then becomes pseudo-first-order with respect to n-butyl bromide, as was also confirmed experimentally:

$$r_2 = k_1 \, c_{BuBr}$$

Description of the system

The quantitative description of the reaction between phenoxide and n-butyl bromide consisted in the determination of the effect of the solvent, of the type of the reagent (sodium and potassium phenoxides), of the ratio of reaction components and of the type of catalyst on the reaction rate.

Effect of solvent. Similarly to the o-allylation of phenol (AKABORI et al. 1978), the reaction rate in the more polar solvent - dichloroethane - is higher than in the nonpolar one - toluene, as demonstrated by the results in Table 1 and as this is usual in the case of the S_N2 reaction. The absolute k_1 values are generally lower due to the lower reaction temperature and the presence of water, and hence to the resulting dissociation of the phenoxide, compared with similar results (McKENZIE and SCHERINGTON 1978) obtained with solid phenoxide in absence of water.

Table I. Effect of the type of solvent and substrate on the rate constant ($k_1(s^{-1})$) of the reaction between phenol and n-butyl bromide
2mmol phenol, 2.548 mmol n-butyl bromide, 0.312 mmol Bu_4NBr, 50°C.

	PhOH, 2.5mol/1NaOH	PhONa
Dichloroethane	$4.34\ 10^{-5}$	$3.95\ 10^{-5}$
Toluene	$1.08\ 10^{-5}$	$1.57\ 10^{-5}$

Effect of the type of reagent. There was no essential difference between the k_1 values if a solution of phenol in 2.5 mol/l NaOH or sodium phenoxide was used (Table II). The k_1 values are however much higher in 2.5 mol/l KOH, due to the higher solubility of potassium hydroxide in the organic phase. While the

Table II. Effect of the type of catalyst (0.311 mmol) on the rate constant ($k_1\ 10^5(s^{-1})$). Reaction conditions cf.Table I.

	Catalyst	Dichloroethane, PhOH 2,5mol/1NaOH		2,5mol/1KOH		Toluene, PhONa	
i	Bu_4NBr	4.34	58.6[a]	12.7	37.3[a]	1.43	10.7[a]
	Dowex 11	0.10	1.3[a]	-		0.36	2.7[a]
	Amberlyst A26	-	-	-		0.20	1.5[a]
ii	PEG 1550	0.29	3.9[a]	-		1.11	8.5[a]
	G-Gel-PEG-600	0.19	2.5[a]	0.75	2.2[a]	0.55	4.2[a]
iii	DB 18C6	-	-	0.44	1.29[a]	0.22	1.6[a]
	DB 18C6-cond.CH_2O	0.46	6.2[a]	0.34	1.0[a]	-	-
	without catalyst	0.074	1.0[a]	0.34	1.0[a]	0.13	1.0[a]

[a] Relative rate constant related to the noncatalyzed reaction.

solubility of NaOH in toluene is lower than 0.009 mmol/ml and in the case of PTC, lower by 0.101 mmol/ml (in dichloroethane 0.038 and 0.140 mmol/ml), the solubility of potassium hydroxide in toluene lies below 0.009 mmol/ml, in the case of PTC below 0.140 mmol/ml. The difference between the activities in the hydroxide used is adequate to that caused by the polar and nonpolar solvent.

Effect of the ratio of reaction components. Since the reaction order is controlled by the solubility of the individual components, it is not possible, by changing their ratio, to assess the reaction order and to determine it by the van't Hoff method within the whole range of concentrations (Fig.2b). At a molar ratio higher than unity in the reaction of phenol in 2.5 mol/l NaOH, k_1 decreases, because the overall alkali concentration is lower than the overall phenol concentration; in the reaction of sodium phenoxide, it is approximately constant, in agreement with the supposed restriction of the reaction by the solubility of components.

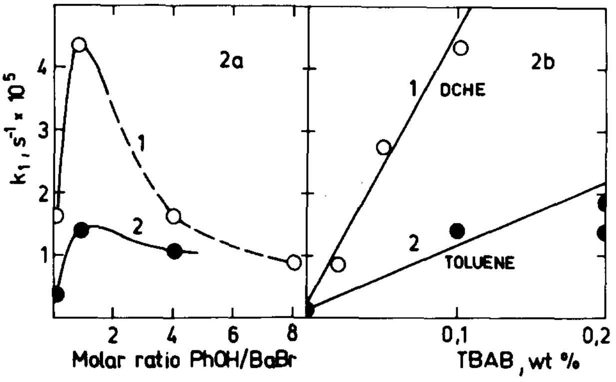

Fig.2 a k_1 (s^{-1}) as a function of the molar ratio PhOH/BuBr, b k_1(s^{-1}) as a function of the concentration of PTC; 1 Dichloroethane, phenol in 2.5 mol/l NaOH, 50°C, 2 Toluene, sodium phenoxide, 50°C

Effect of the type of catalyst. Three groups of PTC were studied:

i quaternary bases
ii coronands
iii polyethyleneglycols,

both in the soluble form and immobilized on the polymer. The results summarized in Table II indicate the following order of reactivities:

in dichloroethane: $Bu_4N^+OH^- > Bu_4N^+Br^- \gg$ DB 18C6 > PEG 1550

in toluene: $Bu_4N^+Br^- \geq$ PEG 1550 > DB 18C6

The catalytic activity of $Bu_4N^+Br^-$ is proportional to the concentration of PTC in the interval 0.0 - 0.2 wt.% (Fig.2b). The reaction order with respect to the catalyst in dichloroethane and in toluene is 0.7 and 0.36 respectively. The decrease is probably due to the lower solubility of the catalyst in toluene.

Immobilization of these types of PTC always leads to a decrease in activity. The smallest decrease in activity due to immobilization takes place in the immobilization of the coronand by condensation with formaldehyde, the largest decrease is observed with quaternary bases; in the latter case, however, the different structure of the functional group and the high degree of substitution of the polymer may become operative. The activity of PEG catalysts may become lower as a result of the possibility of formation of H-bonds, particularly in polar solvents.

The ratio of activities in the polar and nonpolar solvent is not the same, however. The activity of the quaternary base and of coronands is high in polar dichloroethane; on the contrary, polyethyleneglycols are relatively more active in nonpolar toluene. The effect is more pronounced in potassium hydroxide than in sodium hydroxide. In this case, too, the macroporous copolymer is the least active one (Amberlyst A26). It seems that these results also confirm the view that PTC should contain both the hydrophilic and the lipophilic part, in accordance with the reported results (McKENZIE and SHERINGTON 1978).

The lower reaction temperatures used (50°C) enabled the PTC activities to be compared. The higher reaction temperatures (90-110°C) used by preceding authors afface differences between the activities of the catalysts, which made the activity of coronands as PTC to be overestimated.

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