Phase Transfer Catalysts as Co-Catalysts in the Ethoxylation of Nonyl Phenol

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Ethoxylation of nonyl phenol has been carried out at 130°C and at an absolute pressure of two bars. Alkali metal hydroxides were used as catalysts, either neat or in conjunction with added co-catalysts such as 18-crown-6 and tetramethyl ethylene diamine (TMEDA). The overall reaction rates were found to increase five-fold on the addition of the co-catalysts. The use of TMEDA as the sole catalyst gave equally high reaction rates. This fact can be explained by the high basicity of TMEDA and by the formation of a highly reactive ion pair similar to those found in phase transfer catalysis. The differences in the kinetics of the reactions were analysed by computer simulation, using a five parameter model. According to this model, the crown ether-catalyzed ethoxylation of nonyl phenol was found to proceed *via* protonated ethylene oxide, while pure alkali catalysis proceeded mainly *via* uncomplexed ethylene oxide. Small differences in the oligomer distributions were noted.

Alkali catalyzed ethoxylation of phenols and alcohols has been studied extensively, and it is well-known that the kinetics of the reaction depend on the type of catalyst used (1). It has also been shown that the distribution of oligomers can be changed by changing the catalyst (2,3). In a large scale operation, ethoxylation of phenols, e.g., nonyl phenol, is generally carried out in the presence of potassium hydroxide as a catalyst, which gives a high rate of reaction and a Poisson-type distribution of oligomers (1,4).

Alkali catalyzed ethoxylation of phenols and alcohols is believed to proceed through a rate-determining nucleophilic opening of the ethylene oxide ring (1). The reaction rates depend on the nucleophilicity of the phenoxy or alkoxy anions. With anions of low nucleophilicity, activation of the epoxide ring through complex formation with a proton donor may be necessary.

Most ionic reactions in organic media of low polarity proceed through contact ion pairs or solvent separated ion pairs (5,6). The availability of an anion in a nucleophilic displacement reaction depends on the distance between the anion and its positive counter ion. The distance is a function of the effective ionic radii and the charge densities of the ions. By changing to highly polar cation solvating media (e.g., dimethyl sulphoxide or dimethyl formamide) reaction rates of displacement reactions can be increased dramatically. A similar effect can be reached by the use of phase transfer catalysts. The rate increase is correlated to the increased separation of the anion and the solvated cation, and also to the fact that the anion is unsolvated and thus very active (5).

Ethoxylations of phenols and alcohols are generally carried out without any added solvents. The polarity, or cation solvating power, of the reaction medium is very low in the beginning of the reaction. However, as the number of ethylene oxide residues per molecule increases, the cation solvating ability of the medium increases. Oligomers of ethylene oxide are very effective solvating agents for cations (7,8). They are, however, surpassed by phase transfer catalysts such as crown ethers and polyamines.

In the present work we have studied the influence of two auxiliary catalysts [the macrocyclic ether 18-crown-6 and tetramethyl ethylene diamine (TMEDA)] on alkali catalyzed ethoxylation of nonyl phenol. It has previously been shown that the presence of crown ethers increases the rate of alkali catalyzed ethoxylation of alcohols as well as of homopolymerization of ethylene oxide (9–12). However, no detailed study of the effect of phase transfer catalysts on the ethoxylation mechanism has been reported. TMEDA is known to form complexes with lithium ions (13). The use of LiOH/TMEDA or KOH/TMEDA as ethoxylation catalysts has not been previously described in the literature, however.

EXPERIMENTAL

The ethoxylation catalyst (1.22 mole-%) was added to nonyl phenol and the mixture was dehydrated under vacuum (20 mm Hg) at 80°C on a thin film evaporator. The appropriate co-catalyst was added (18-crown-6: 1 mole/mole; TMEDA: 2 moles/mole), and ca. 400 g of the mixture, corresponding to 1.8 moles of nonyl phenol, was weighed into a stainless steel autoclave that was equipped with a high speed stirrer. In the experiment with TMEDA as the main catalyst the same amount (2.44 mole-%) as previously used was employed. The autoclave was leak tested at five bars with N_2 and then evacuated. The temperature was increased to 130°C. Ethylene oxide was then admitted to the autoclave at zero time. The pressure was manually kept between 1.95 and 2.0 bars by periodically charging ethylene oxide into the autoclave. The amounts of ethylene oxide charged and the corresponding reaction times were recorded. The addition of ethylene oxide was interrupted when three moles of ethylene oxide per mole of nonyl phenol had been added. The reaction was allowed to proceed at 130°C until the pressure reading decreased to the starting value. After cooling the mixture to room temperature, the autoclave was evacuated in order to remove ethylene oxide, flushed with N_2 and dismantled. The oligomer distribution of the reaction products were determined by gas chromatography after silylation. Hydroxyl values of the reaction products were found to generally correspond to 90% conversion of ethylene oxide (2.7 moles EO/mole of nonyl phenol).

RESULTS AND DISCUSSION

Effect of catalysts. Nonyl phenol was ethoxylated at

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130°C at a pressure of two bars. Potassium and lithium hydroxides were used as catalysts, either neat or with 18-crown-6 or TMEDA as co-catalysts. A reaction was also run with TMEDA as the sole catalyst. For comparison, nonyl phenoxyethyl alcohol was ethoxylated with potassium hydroxide/18-crown-6 as a catalyst. The consumption of ethylene oxide was recorded

as a function of time. The experimental results are shown in Figures 1, 2, and 3. The ethylene oxide consumption curves for the ethoxylation of nonyl phenol clearly show three separate kinetic regions. These regions correspond to an initial fast physical absorption of ethylene oxide, a slow ethoxylation of nonyl phenol to nonyl phenoxyethyl alcohol (phenol → EO_1), and a
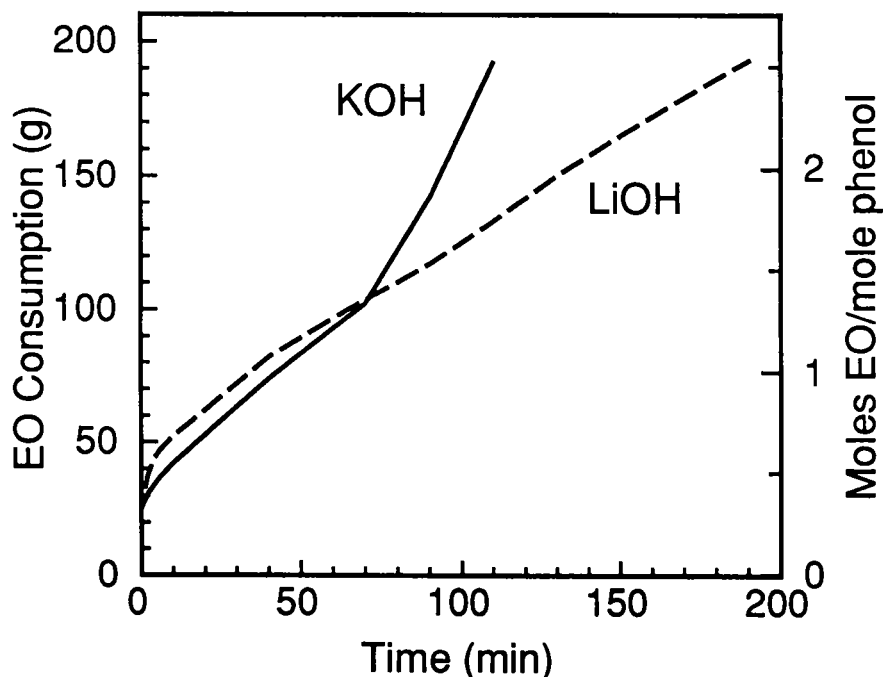

FIG. 1. Ethoxylation of nonyl phenol in the presence of KOH and LiOH. Catalyst concentration 1.2 mole-%, temperature 130°C. EO pressure 2 bars.
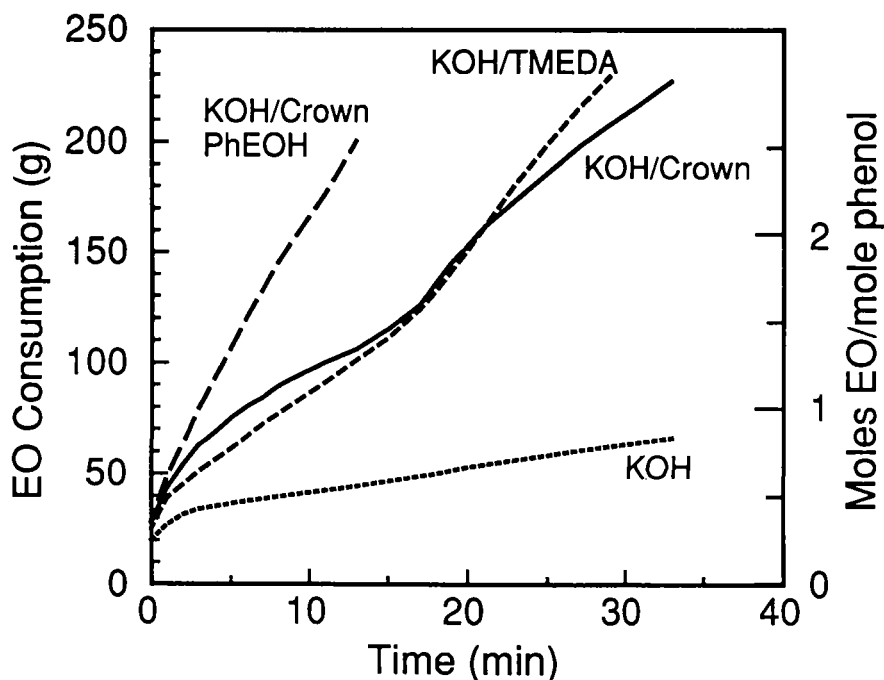

FIG. 2. Ethoxylation of nonyl phenol in the presence of KOH, KOH/18-crown-6 (1:1), and KOH/TMEDA (1:2), and ethoxylation of nonyl phenoxyethyl alcohol (PhEOH) in the presence of KOH/18-crown-6 (1:2). Catalyst concentration 1.2 mole-%, temperature 130°C. EO pressure 2 bars.

fast oligomerization reaction ($EO_n \rightarrow EO_{n+1}$). This is in accordance with the accepted view that no ethoxylation of the phenoxyethyl alcohol that is formed in the first reaction step will take place until all of the more acidic phenol is consumed (1). The oligomerization then follows at a higher rate due to the high nucleophilicity of the alkoxide anions (Figure 1).

The lithium hydroxide catalyzed reaction was slower than the potassium hydroxide reaction, as can be expected because of the smaller size and higher charge density of the lithium ion (Figure 1). The effect is pronounced in the second part of the reaction. The rate of oligomerization is similar to the rate of the initial phenol ethoxylation, and lower by a factor of three than the rate of the corresponding potassium catalyzed oligomerization reaction.

The use of 18-crown-6 as a co-catalyst was found to have a marked effect on the rate of the KOH catalyzed ethoxylation. As can be seen from Figure 2, the presence of the crown ether in equimolar amounts to potassium ions gave a five-fold increase in the overall reaction rate. This effect can be explained by the formation of a strong 1:1 complex between potassium ions and 18-crown-6. The complex formation increases the effective radii of the cations and leaves the anions naked and highly reactive (5). It can be noted that preformed nonyl phenoxyethyl alcohol was found to react with ethylene oxide at a rate corresponding to that of the second part of nonyl phenol ethoxylation (Figure 2).

The results obtained with TMEDA as a co-catalyst were somewhat unexpected. As shown in Figure 2, the overall reaction rate obtained with KOH/TMEDA as a catalyst was similar to that obtained with KOH/18-crown-6. There is, however, a significant difference in the curvatures of the first part of the ethylene oxide consumption curves, which indicates a difference in the reaction mechanisms. The curve obtained with LiOH/TMEDA as a catalyst was similar to that obtained for KOH/TMEDA (Figure 3). In both cases, the rates of the second part of the reactions seem to decrease with time.

The behavior of TMEDA as an ethoxylation catalyst was tested. It has previously been reported that TMEDA in relatively large concentrations can catalyze the ethoxylation of butanol (14). The results shown in Figures 2 and 3 point out that TMEDA alone is as effective a catalyst as either LiOH/TMEDA or KOH/TMEDA. We suggest the following explanation for this behavior.

TMEDA is a strong base due to the possibility of binding a proton in a five-membered ring (15). In the systems studied, protonation of the diamine will compete with the formation of the alkali metal ion complex. With a comparatively strong acid such as an alkyl phenol, protonation will dominate and phenolate ions will be formed, as shown in Scheme 1 (Eqn. 1). The phenolate ions will subsequently react with ethylene oxide to form nonyl phenoxyethyl alcohol. This product, being a weaker acid than the alkyl phenol, will not protonate TMEDA to any appreciable extent. TMEDA will now be free to form the alkali metal ion complex. However, it will also be capable of reacting with ethylene oxide, forming a zwitterion which can react further with ethylene oxide to give higher homologues (Eqns. 4,5).

The zwitterion formed according to Scheme 1 will undergo rapid equilibrium with the nonyl phenoxyethyl alcohol formed in the previous step (Scheme 2, Eqn. 1). For $n=0$ this equilibrium will be shifted to the left
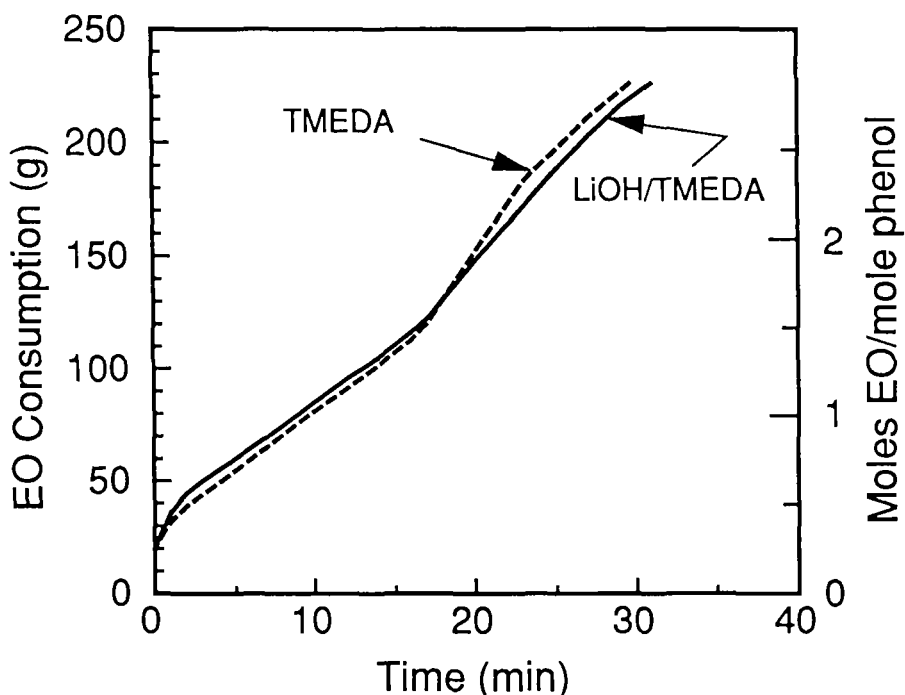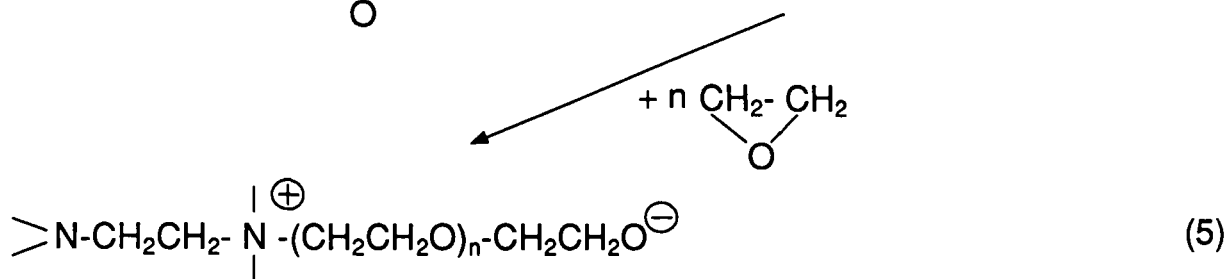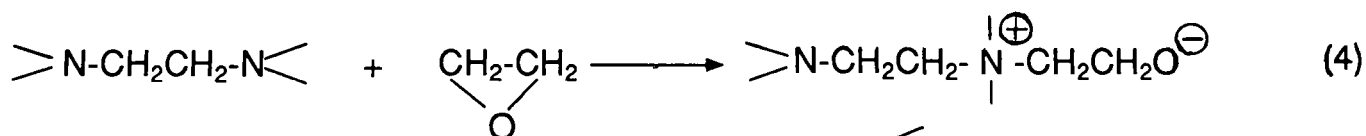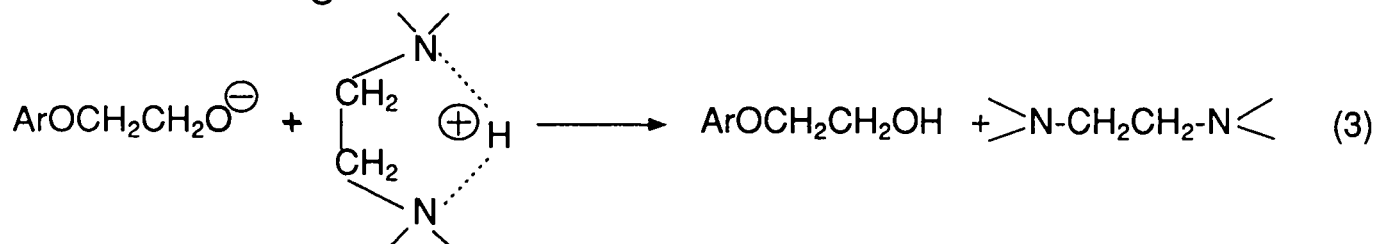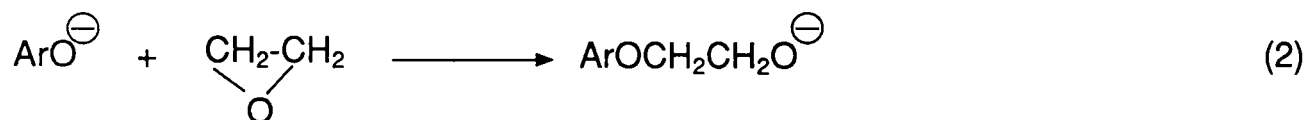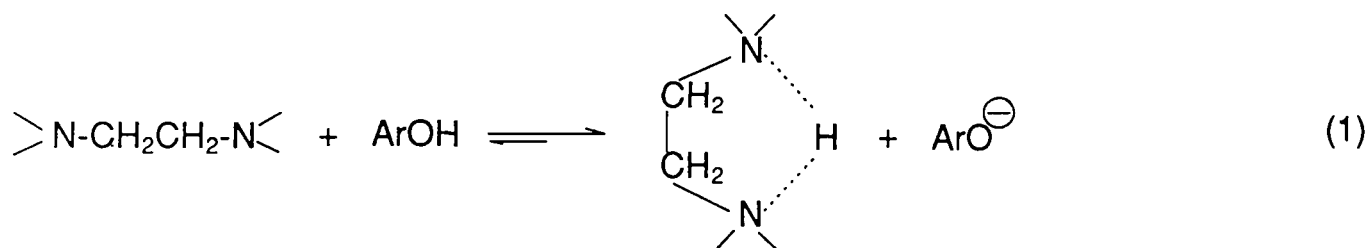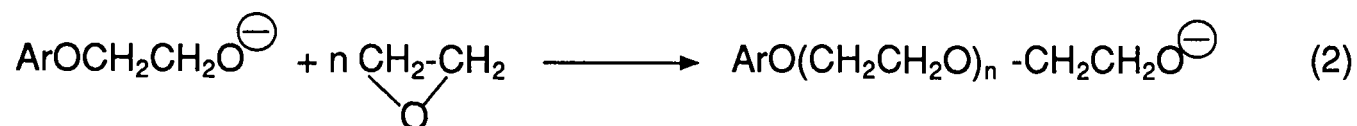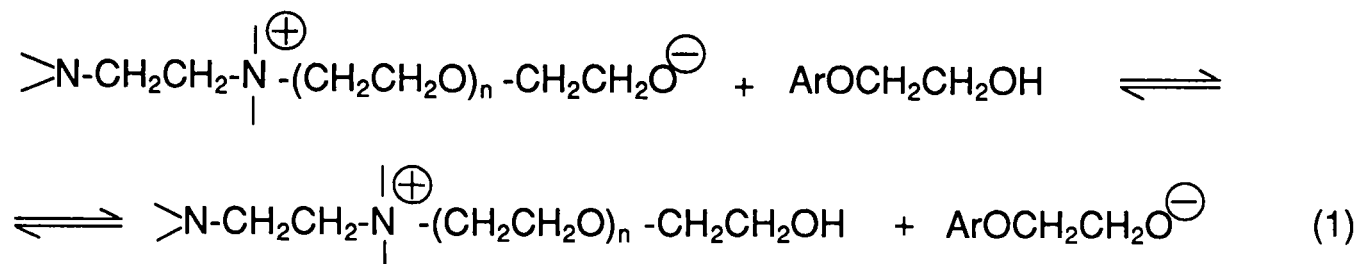

FIG. 3. Ethoxylation of nonyl phenol in the presence of LiOH/TMEDA (1:2) and TMEDA. Catalyst concentrations 1.2 and 2.4 mole-%, respectively. EO pressure 2 bars.

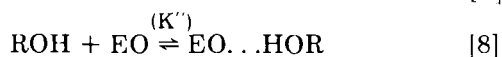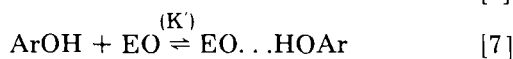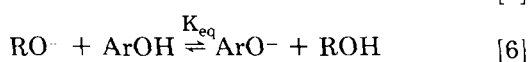$$>N-CH_2CH_2-N< \ + \ ArOH \ \Longrightarrow \ \begin{array}{c} N \\ CH_2 \\ CH_2 \\ N \end{array} H \ + \ ArO^{\ominus} \qquad (1)$$

$$ArO^{\ominus} \ + \ \underset{O}{CH_2-CH_2} \ \longrightarrow \ ArOCH_2CH_2O^{\ominus} \qquad (2)$$

$$ArOCH_2CH_2O^{\ominus} \ + \ \begin{array}{c} N \\ CH_2 \\ \oplus H \\ CH_2 \\ N \end{array} \ \longrightarrow \ ArOCH_2CH_2OH \ + >N-CH_2CH_2-N< \qquad (3)$$

$$>N-CH_2CH_2-N< \ + \ \underset{O}{CH_2-CH_2} \ \longrightarrow \ >N-CH_2CH_2-\overset{\oplus}{\underset{|}{N}}-CH_2CH_2O^{\ominus} \qquad (4)$$

$$+ \ n \ \underset{O}{CH_2-CH_2}$$

$$>N-CH_2CH_2-\overset{\oplus}{\underset{|}{N}}-(CH_2CH_2O)_n-CH_2CH_2O^{\ominus} \qquad (5)$$

SCHEME 1

$$>N-CH_2CH_2-\overset{\oplus}{\underset{|}{N}}-(CH_2CH_2O)_n-CH_2CH_2O^{\ominus} \ + \ ArOCH_2CH_2OH \ \Longrightarrow$$

$$\Longrightarrow \ >N-CH_2CH_2-\overset{\oplus}{\underset{|}{N}}-(CH_2CH_2O)_n-CH_2CH_2OH \ + \ ArOCH_2CH_2O^{\ominus} \qquad (1)$$

$$ArOCH_2CH_2O^{\ominus} \ + \ n \ \underset{O}{CH_2-CH_2} \ \longrightarrow \ ArO(CH_2CH_2O)_n-CH_2CH_2O^{\ominus} \qquad (2)$$

SCHEME 2

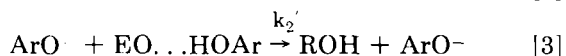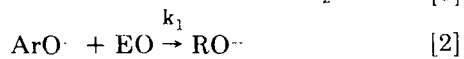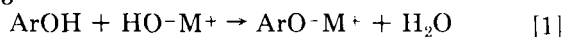because the 2-ammoniumethyl alcohol is more acidic than the 2-aryloxyethyl alcohol. For n>1 the situation is reversed—the 2-aryloxy alcohol is now the stronger acid, although the acidity difference might be small. The alkoxide formed will be further ethoxylated to form the normal distribution of homologues, as shown in Scheme 2 (Eqn. 2).

In the final reaction step in Scheme 2 (i.e, ethoxylation of the 2-aryloxy alkoxide) the ethoxylated TMEDA is likely to function as the cationic moiety of the propagating ion pair. Because of the bulkiness of the cation the charge centra of the ion pair will be well separated, giving a highly reactive anion. The suggested reaction mechanism explains why the rate of TMEDA catalyzed ethoxylation is much higher than that of a normal alkali catalyzed reaction. It also accounts for the fact that the combination of alkali hydroxide and TMEDA offers no advantage over TMEDA alone.

Ethoxylation kinetics. A simple kinetic model can be used for the analysis of the ethylene oxide consumption curves. Base catalyzed ethoxylation of a phenol may proceed according to Scheme 3. In this model, phenolate anions can react with either uncomplexed (Eqn. 2) or complexed ethylene oxide (Eqn. 3). Phenoxyethyl alkoxide (or oligomers) reacts similarly (Eqns. 4,5). All ethylene oxide oligomers (ROH) are presumed to have equal reactivity. The protonation equilibrium in Equation 6 is presumed to be shifted far to the right, i.e., the equilibrium constant K_{eq} assumes a high value. Equilibrium constants K' and K'' are incorporated into rate constants k_2 and k_4. For reasons of simplicty concentrations are expressed as moles•kg^{-1}.

Scheme 3

$$ArOH + HO\text{-}M^+ \rightarrow ArO\text{-}M^+ + H_2O \qquad [1]$$

$$ArO^- + EO \xrightarrow{k_1} RO^- \qquad [2]$$

$$ArO^- + EO...HOAr \xrightarrow{k_2'} ROH + ArO^- \qquad [3]$$

$$RO^- + EO \xrightarrow{k_3} RO^- \qquad [4]$$

$$RO^- + EO...HOR \xrightarrow{k_4'} ROH + RO^- \qquad [5]$$

$$RO^- + ArOH \underset{}{\overset{K_{eq}}{\rightleftharpoons}} ArO^- + ROH \qquad [6]$$

$$ArOH + EO \overset{(K')}{\rightleftharpoons} EO...HOAr \qquad [7]$$

$$ROH + EO \overset{(K'')}{\rightleftharpoons} EO...HOR \qquad [8]$$
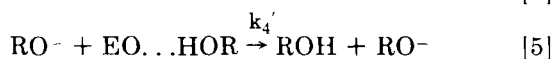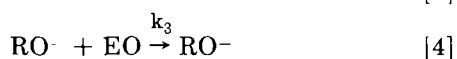
In the reaction scheme ROH stands for *any* ethylene oxide oligomer, regardless of the degree of polymerization. The following equations can be derived from the reaction scheme:

$$R_1 = k_1 \cdot C_{ArO^-} \cdot P_{EO} + k_2 \cdot C_{ArO^-} \cdot C_{ArOH} \cdot P_{EO}$$

$$R_2 = k_3 \cdot C_{RO^-} \cdot P_{EO} + k_4 \cdot C_{RO^-} \cdot C_{ROH} \cdot P_{EO}$$

$$R = R_1 + R_2$$

$$C_{ArO^-} + C_{RO^-} = C_M$$

$$C_{ArO^-} \cdot C_{ROH}/(C_{RO^-} \cdot C_{ArOH}) = K_{eq}$$

where R, R_1, R_2 = reaction rates expressed as EO consumption (moles•kg^{-1}•s^{-1});

$k_1; k_3$ ($bar^{-1} \cdot s^{-1}$)

$k_2 = k_2' \cdot K'; k_4 = k_4' \cdot K''$ (kg • bar^{-1} • mol^{-1} • s^{-1}).

C_{ArO^-}, C_{RO^-}, etc. = instantaneous concentrations of ArO^-,

RO^-, etc. (moles • kg^{-1});

C_M = concentration of added catalyst, i.e., KOH (moles • kg^{-1});

P_{EO} = partial pressure of ethylene oxide (bars). The partial pressures of ethylene oxide were substituted for concentrations in the rate equations. P_{EO} is held constant during the experiment.

Because the reactor used was of the semi-batch type, the weight (or volume) of the reactor charge is a function of time. The instantaneous concentrations will then be expressed as:

$$C_{ArOH} = N_{ArOH}/W \text{ (moles • } kg^{-1}); W = W_0 + W_{EO} \text{ (kg)};$$

W_{EO} = weight of added ethylene oxide, and

W_0, W = initial and instantaneous weight of the charge.

The equations above were used for a computer simulation of the ethylene oxide consumption curves. A special simulation software, SIMNON, was used with a DEC VAX computer (Digital Equipment Corp.) (16). The rate constants k_1, k_2, k_3, and k_4, together with the equilibrium constant K_{eq}, were used as parameters for the simulation. Figure 4 displays experimental and simulated curves for KOH, KOH/18-crown-6, and TMEDA. In the case of TMEDA it was assumed that the entire catalyst was active as a base ($C_M = C_{TMEDA}$). The parameters found to give the best fit are shown in Table 1. It is clear that the simple kinetic model used can describe the system in all three cases. The difference in curvature between the different EO consumption curves depends on the relative magnitude of the constants k_1 and k_2. The crown ether catalyzed ethoxylation of nonyl phenol seems to proceed mainly *via* protonated ethylene oxide, as is indicated by the high value obtained for k_2. In the other two cases the unprotonated route seems to dominate.

In the reactions catalyzed by KOH/crown ether and TMEDA there is a gradual rate decrease after the addition of 1.5 to 2 moles of EO per mole nonyl phenol. The lower rate might be an effect of dilution due to added EO, but the rate decrease is larger than the dilution effect expected for a pseudo second order rate equation (Eqn. 4). It seems more likely to assume that the longer homologues react at a lower rate than the short ones, i.e., the presumption of equal reactivity might not be valid. The experimental oligomer distributions would then differ from the theoretical Poisson-type distribution. The experimental distributions ob-

tained in the presence of crown ether and TMEDA seem to be slightly more narrow than those obtained in the normal alkali catalyzed reaction. The differences are small, and close to the experimental errors. However, all distributions are distinctly more narrow than the Poisson distribution, and this is in agreement with the view that the reactivity of the oligomers decrease with the chain length (17).
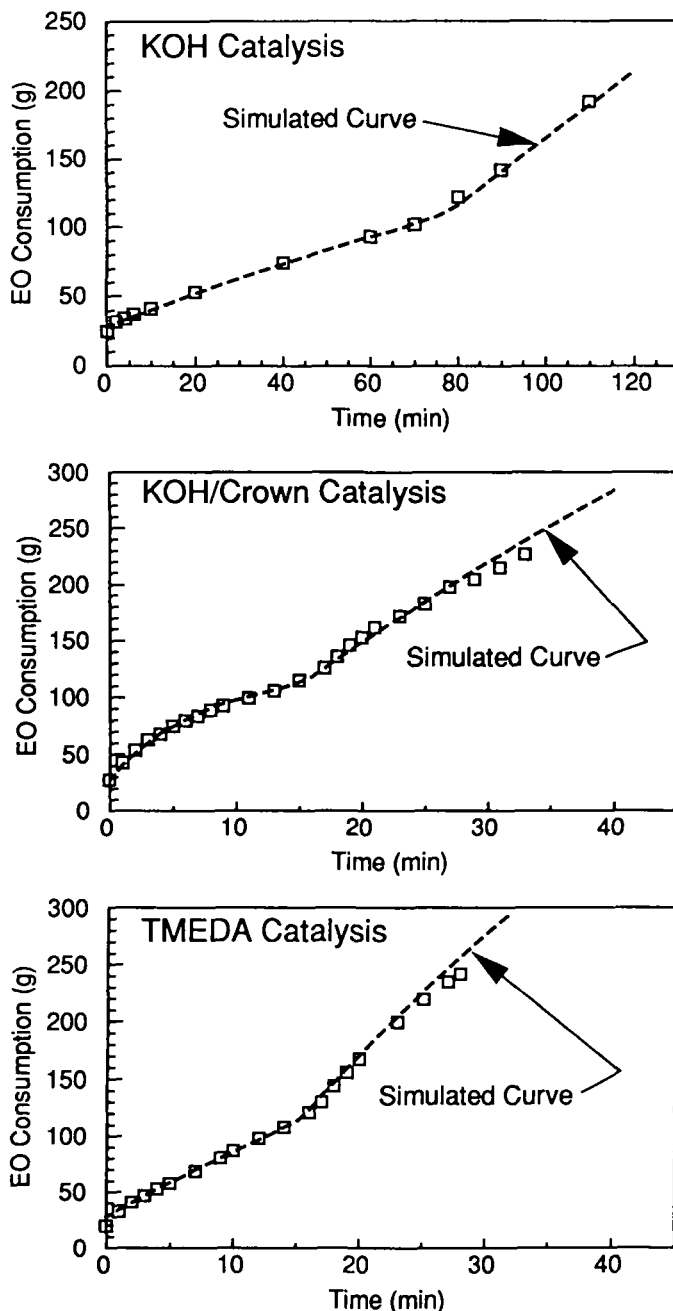

FIG. 4. Experimental (open squares) and computer simulated (dashed line) ethylene oxide consumption curves for KOH, KOH/ 18-crown-6, and TMEDA.

TABLE 1

Parameters used for computer simulation of ethylene oxide consumption curves in Figure 4.

Catalyst (Parameter)	KOH	KOH-CROWN	TMEDA
k_1 $(s^{-1} \cdot bar^{-1})$	$7.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
k_2 $(kg \cdot s^{-1} \cdot bar^{-1} \cdot mole^{-1})$	$7.5 \cdot 10^{-4}$	$2.7 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$
k_3 $(s^{-1} \cdot bar^{-1})$	$2.1 \cdot 10^{-2}$	0.0	0.0
k_4 $(kg \cdot s^{-1} \cdot bar^{-1} \cdot mole^{-1})$	0.0	$2.0 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$
K_{eq}	300	100	100

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