The Lithium Phenoxide Catalyzed Addition
of Propylene Oxide to Phenol

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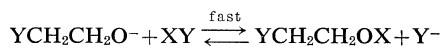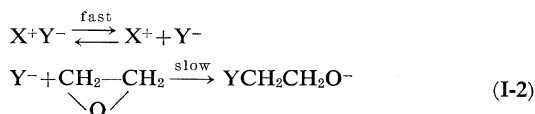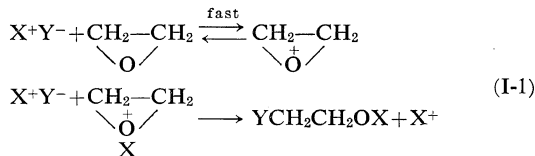München, Germany.

ABSTRACT: Addition of propylene oxide to phenol with lithium phenoxide as a catalyst was studied under various temperature as well as composition conditions. The kinetic study of this reaction rules out an ionic mechanism and proposes instead a multi-centred reaction in which the three component associated transition complex re-arranges to yield reaction products. Arrhenius parameters in the case of lithium phenoxide exhibit marked deviations from those of homologue alkali phenoxides: there is an abrupt and unusually high decrease in the activation energy accompanied by a corresponding decrease in the frequency factor, the reaction velocity remaining almost unchanged. This compensation effect takes place as a result of a multi-centred reaction in homogeneous phase.
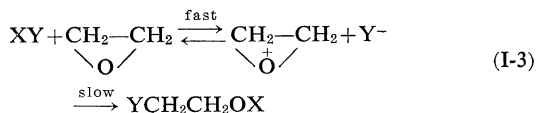KEYWORDS   Lithium Phenoxide / Phenol / Propylene Oxide / Addition /
Kinetics / Multicentred Reaction / Base-Catalyzed /

A large number of reactions of alkylene oxides have been studied[1], and most of them involve opening of the epoxide ring. On account of the strain in three-membered ring compounds, the 1, 2-epoxides are capable of adding, similar to carbonyl groups, however reversible, polar compounds, whereby the bond to be broken is the carbon—oxygen bond of highly polar nature. The cleavage of epoxides can be made to result through the agency of a variety of catalysts under appropriate conditions in polymerization.

Ring-opening reactions of the epoxide ring may be summarized in schemes I-1 to I-3, in which X^+Y^- represents an ionic agent.

$$X^+Y^- + CH_2\!\!-\!\!CH_2 \underset{}{\overset{fast}{\rightleftarrows}} CH_2\!\!-\!\!CH_2$$
$$ \diagdown O \diagup \diagdown \overset{+}{O} \diagup$$

$$X^+Y^- + CH_2\!\!-\!\!CH_2$$
$$ \diagdown \overset{+}{O} \diagup \longrightarrow YCH_2CH_2OX + X^+ \quad (I\text{-}1)$$
$$ X$$

$$X^+Y^- \overset{fast}{\rightleftarrows} X^+ + Y^-$$

$$Y^- + CH_2\!\!-\!\!CH_2 \overset{slow}{\longrightarrow} YCH_2CH_2O^-$$
$$ \diagdown O \diagup (I\text{-}2)$$

$$YCH_2CH_2O^- + XY \overset{fast}{\rightleftarrows} YCH_2CH_2OX + Y^-$$

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* A. Hussain, D. Sc. Thesis, Technische Universität, München, 1970.

$$XY + CH_2\!\!-\!\!CH_2 \overset{fast}{\rightleftarrows} CH_2\!\!-\!\!CH_2 + Y^-$$
$$ \diagdown O \diagup \diagdown \overset{+}{O} \diagup (I\text{-}3)$$
$$\overset{slow}{\longrightarrow} YCH_2CH_2OX$$

In every case the process of ring opening is the rate-determining step and the reactions, therefore, follow an S_{N2} mechanism. A few studies on the acid-catalysed hydrolysis of alkylene oxides seem to favour an S_{N1} mechanism,[2,3] but the ambiguity of the conclusions of these studies has also been pointed out. Of the above-mentioned three types of ionic reactions, I-1 is related to the cationic polymerization of epoxides, and I-2 to the anionic polymerization. The first extensive work on the mechanism of cationic polymerization of ethylene oxide with $SnCl_4$ and BF_3 as catalyst has been reported.[4,5] It can be concluded from their studies that each $SnCl_4$ molecule rapidly initiates two polymer chains which slowly increase in length through stepwise addition of the monomer. The polymerizations of epoxides by Lewis acids are highly complex and cannot be treated simply in terms of cationic polymerization.

In the base-catalysed polyadditions of epoxides to alcohols with alkali alkoxides as catalyst, two distinct fundamental reactions are involved: one
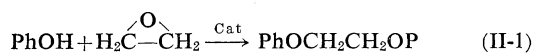
is addition of the first epoxide molecule to alcohol and the other is the successive addition of the monomer epoxide to the product—alcohols that have hydroxyalkyl end groups.
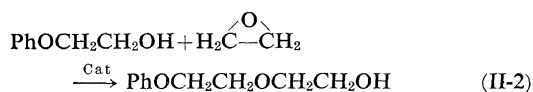
The base-catalysed ring-cleavage of epoxides in solution has long since been reported to follow a bimolecular ionic mechanism.[6,7] Patat and coworkers[8,9] have, however, contradicted an ionic mechanism for the above reaction; they proposed a modified mechanism in which a complex reaction takes place *via* a ternary transition aggregate formed by the reaction partners. Moreover it has been shown that alkali alkoxides do not react with epoxides in the absence of proton active compounds like alcohols. The catalyst—substrate complex of alkoxide with epoxide—alcohol adduct results in the following reaction products which are formed *via* route analogous to the Michaelis—Menten-fermentation reaction.

ROH . . . Epoxide+Cat

$\rightleftharpoons$ ternary complex $\longrightarrow$ monoether+Cat
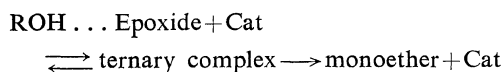
All of the three reactants are believed to exercise the rate-determining effect on the reaction. The kinetics of the initiation and propagation steps of this reaction have not been studied to any great extent. Patat, *et al.*, have reported the kinetics of the first two steps in the sodium phenoxide catalysed polymerization of ethylene oxide: they found that reaction II-1 proceeded to completion

$$PhOH + H_2C\overset{O}{\underset{}{-}}CH_2 \xrightarrow{Cat} PhOCH_2CH_2OP \qquad (II\text{-}1)$$

before the subsequent addition (II-2) takes place

$$PhOCH_2CH_2OH + H_2C\overset{O}{\underset{}{-}}CH_2$$

$$\xrightarrow{Cat} PhOCH_2CH_2OCH_2CH_2OH \qquad (II\text{-}2)$$

This may be due to the fact that phenol activates ethylene oxide to a greater extent in the coordination complex than does the produced alcohol because the former is more acidic than the latter. Further, the reaction is of the first order with respect to sodium phenoxide; the reaction order with respect to phenol coverges from first order at low concentration to zero order at high concentration. The reaction rate is independent of ethylene oxide concentration, pro-

vided the epoxide is present in molar excess. Alkali oxides have been reported to catalyse with a first order reaction.[10] A likewise multi-centered mechanism was proposed by Sakai and Ishii[11] for the reaction of substituted phenol and epoxide with phenoxide as catalyst. In the following paper a kinetic study of addition of propylene oxide to phenol in the presence of lithium phenoxide as a catalyst has been reported. Whereas for the PhOLi-catalysed addition of ethylene oxide to phenol a valid rate-law could be derived, an application of this rate-law on the system phenol/propylene oxide/lithium phenoxide under otherwise similar conditions falls short of expectations. In the case of propylene oxide the concentration of PhOLi in this manner has been selected because there was no first order for the catalyst.

RESULTS

The addition of propylene oxide to phenol in the presence of lithium phenoxide as catalyst was carried out in excess of propylene oxide at (a) various PhOH : PO molar ratios under constant reaction temperature and (b) different reaction temperatures, keeping PhOH : PO molar ratio constant.

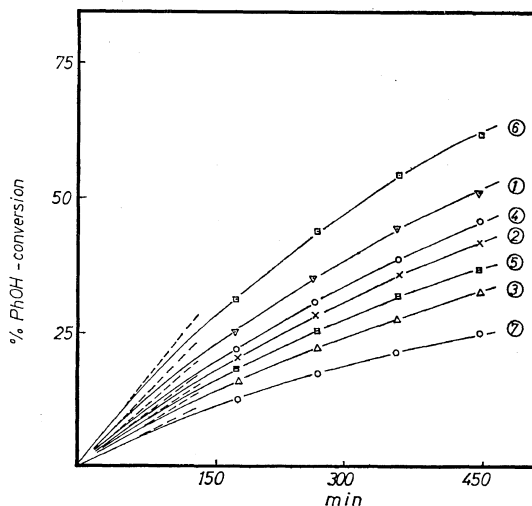The reaction rate-curves based on the consumption of phenol show that the rate of addition

Figure 1. Conversion—time curves: series B, temp, 70°C; molar ratio PhOH : PO = 1 : 2.

of propylene oxide increases exponentially with time. The results of one particular reaction series are shown in Figure 1. Other series follow similar behaviour. It can be seen from Figure 1 as well as Table I that the rate of addition

Table I. Influence of catalyst concentration on the over-all reaction-rate

Series A[a]

Expt no.	Catalyst $\times 10^2$, mol/l	$v_0 \times 10^4$, min^{-1}	$v_0' \times 10^3$, mol/l min
7	2.112	7.16	3.05
3	3.420	9.43	3.965
5	4.297	10.4	4.36
2	5.81	12.0	5.03
4	7.089	13.3	5.57
1	8.99	15.00	6.28
6	16.64	18.30	7.66

[a] Temp, 70°C; PO, 8.374 mol/l; PhOH$_0$, 4.187 mol/l; d_{70}, 0.8810.

increases directly with the catalyst concentration. In order to determine the order of reaction with respect to each component, the initial rate method was applied. The value of initial rate (*i.e.*, the value of dx/dt from concentration—time data can be cal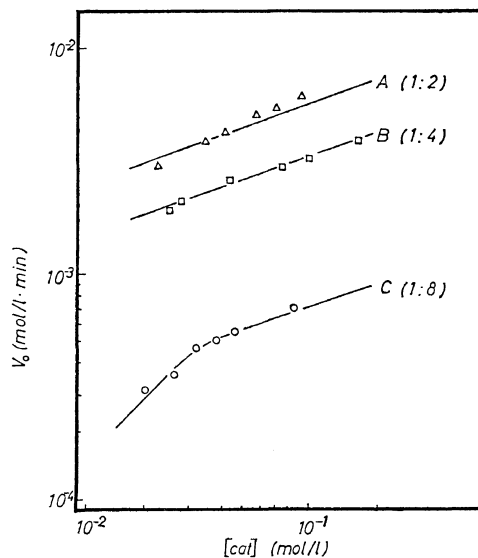culated by laying tangents along the curve at zero time *i.e.*, at $t=0$ and measuring its slope. By plotting $\log dx/dt$ *versus* corresponding log values of catalyst concentration, a straight line is obtained, where the slope yields reaction order with respect to lithium phenoxide and tends to be 1/3 (see Figure 2—3).
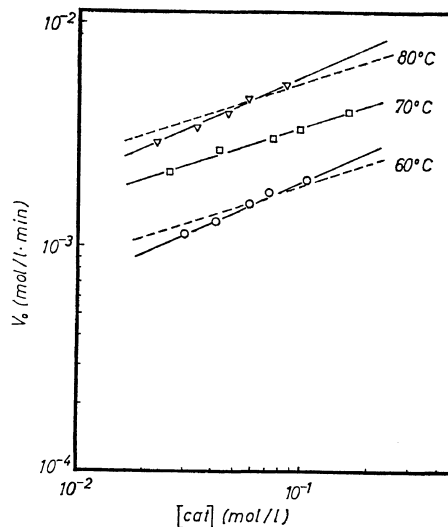

Figure 3. Order of reaction with respect to lithium phenoxide at several temperatures; molar ratio, 1 : 4.

Influence of Molar Ratio PhOH : PO on the Rate of PO-Addition

Since phenol also takes part in the rate determining process, it is of particular interest here to investigate the effect of concentration of phenol on the over-all reaction. For this purpose the reaction was carried out at molar ratios PhOH :

Figure 2. Order of reaction with respect to lithium phenoxide in parenthesis the different molar ratios phenoxide of PhOH to PO.

Table II. Influence of catalyst concentration on the over-all reaction-rate

Series B[a]

Expt no.	Catalyst $\times 10^2$, mol/l	$v_0 \times 10^4$, min^{-1}	$v_0' \times 10^3$, mol/l min
6	2.357	7.80	1.95
5	2.610	8.3	2.13
1	4.303	10.33	2.65
2	7.415	12.0	3.08
3	9.960	13.10	3.36
4	16.340	15.30	3.925

[a] Temp, 70°C; PO$_0$, 10.254 mol/l; PhOH$_0$, 2.562 mol/l; d_{70}, 0.8410.

Table III. Influence of catalyst concentration on the over-all reaction-rate

Series C[c]

Expt no.	Catalyst $\times 10^2$, mol/l	$v_0 \times 10^4$, min^{-1}	$v_0' \times 10^3$, mol/l min
6	1.880	2.18	0.314
2	2.390	2.46	0.354
4	3.180	3.3	0.475
3	3.860	3.53	0.508
1	4.590	3.83	0.556
5	8.760	4.71	0.678

[c] Temp, 70°C; PO_0, 11.52 mol/l; $PhOH_0$, 1.44 mol/l; d_{70}, 0.8080.

PO between 1 : 2—1 : 8, the temperature being kept constant at 70°C. Tables I—III clearly show that the over-all reaction-rate, calculated on the basis of unit catalyst concentration, increases directly with the phenol concentration (see last column of Tables I—III).

From the reaction series A, B, and C appropriate data were derived to study the effect of phenol concentration on the over-all reaction. By recalculating from these series the molar PhOH-concentration based on the catalyst amount of 0.05 mol/l, log [PhOH]$_0$ was plotted *versus* corresponding values of log V_0. Figure 4 shows how the order of phenol changes from 1 at low concentration to zero at higher concentration.
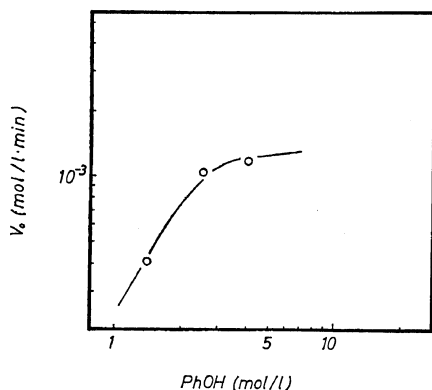

Figure 4. Order of reaction with respect to phenol.

Influence of Temperature and Activation Energy

In order to determine the apparent activation energy E_a of the reaction, experiments were conducted at different temperatures 60, 70, and 80°C, keeping the molar ratio PhOH : PO constant at 1 : 4. Extrapolation of curves in Figure 3 yields necessary reaction-rate constants, which are plotted, logarithmically *versus* 1/T in Figure 5. From the slope of the log k *vs*. 1/T-curve the
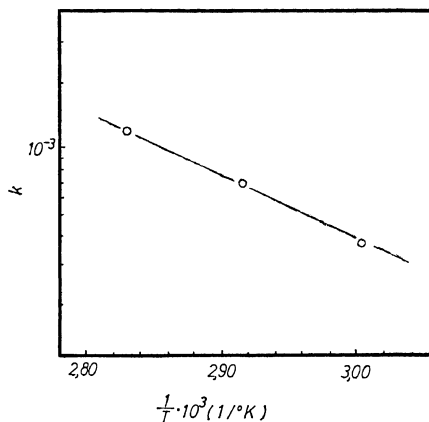

Figure 5. Arrhenius plot.

apparent activation energy has been calculated to be 10.6 kcal/mol. This value of activation energy, as compared to 14.4 kcal/mol of sodium phenoxide/propylene oxide/phenol system, seems to be a bit too low. A lower value of E_a should, according to the equation $k = A \exp(-E_a/RT)$ result in a rise in the rate constant k; however, in the case of lithium phenoxide the lowering of E_a is not accompanied by corresponding increase in k-value because k is as a matter of fact smaller for our system. The value of A calculated from log k—1/T-curve shows again a considerable fall for LiOPh and amounts to 8.97×10^2 sec^{-1}. There is, therefore, a marked reduction in activation energy in the case of lithium phenoxide which is compensated and accompanied by a corresponding decrease in the frequency factor A as well as in the activation entropies term$\Delta S^{\neq}$ which is calculated to be -39.3 cal/mol deg.
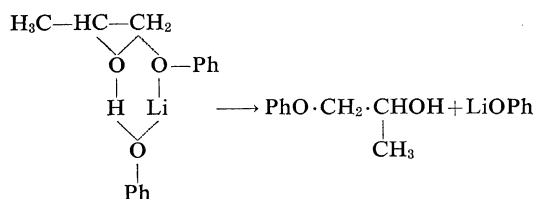
DISCUSSION

A simple bimolecular, anionic mechanism proposed by, among others, Boyd and Marle[12] for the base-catalysed epoxide cleavage has already been contradicted by Patat and cowork-

ers.[8,9] The unusual high negative value of activation volume[13] for caesium phenoxide catalysed propylene oxide cleavage also rules out an ionic mechanism and supports complex reaction taking place *via* a ternary transition aggregate. If we take the ionic mechanism of Weibull[7] for granted, phenol should show a constant-order participation in our reaction. However, phenol has been found to change the reaction order from 1 at lower concentration to zero at high concentration.* The kinetic study for the reaction PhOLi/PO/PhOH at different molar ratios of PhOH/PO confirms the necessity of the existence of a proton active component from which PhOH is liberated by the cleavage. The extent to which concentration of the catalyst or phenol influences the rate of reaction depends upon the state of equilibrium between the ternary complex and the reaction partners.
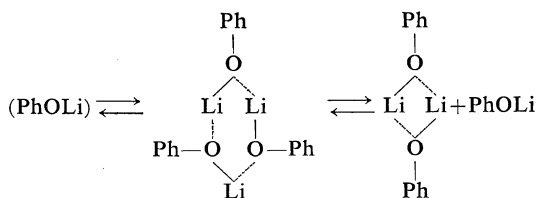
PhOH . . . PO+PhOLi $\rightleftharpoons$ transition complex
$\longrightarrow$ reaction product+PhOLi
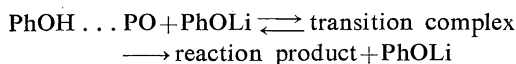
The transition complex decays to yield the reaction product in the following manner

$$H_3C—HC—CH_2$$

$$\begin{array}{cc} O & O—Ph \\ | & | \\ H & Li \\ \end{array} \longrightarrow PhO \cdot CH_2 \cdot CHOH + LiOPh$$
$$\begin{array}{c} O \\ | \\ Ph \end{array} \qquad\qquad \begin{array}{c} | \\ CH_3 \end{array}$$

The mutual influence of phenol and the catalyst activates the decay of the ternary complex.

Wittmann[10] as well as Itakura[14] found first order with respect to the catalyst sodium phenoxide and on this basis they assumed a first-order reaction for the homologue lithium phenoxide. Our results, however, show that lithium phenoxide takes part in the reaction PO/PhOH /PhOLi with an order which tends to be 1/3. This anomaly in the case of PhOLi can be justified by picturing it as a trimer form in equilibrium with the monomer and dimer form as follows

$$(PhOLi) \rightleftharpoons \begin{array}{c} Ph \\ | \\ O \\ Li \; Li \\ | \; | \\ Ph—O \; O—Ph \\ Li \end{array} \rightleftharpoons \begin{array}{c} Ph \\ | \\ O \\ Li \; Li+PhOLi \\ O \\ | \\ Ph \end{array}$$

This state of equilibrium obviously depends upon the concentration of lithium phenoxide in the reaction mixture. As expected, the order of reaction with respect to PhOLi changes with decreasing concentration of the catalyst from 1/3 to 1. Since the decreasing in catalyst concentration corresponds to shift from trimer to monomer, transition is accordingly observed in the reaction order curve for PhOLi (Figure 2). Of the various forms of the catalyst that are available depending upon the equilibrium state, the monomer form is believed to initiate the cleavage.

A 1/3 order with respect to sodium and potassium phenoxide is also expected to appear if the catalyst is employed in sufficiently high concentration. Apparently, it is not possible to achieve the appropriate solubility range for PhONa and PhOK. Organometallic compounds of lithium, owing to small Li-ionic radius, tend to associate if they are present in large concentration. Worsfold and Bywater[15] have presented for BuLi-catalysed polymerization of styrene a rate-law, which has been interpreted to suggest the existence of the catalyst in the associated hexamer form $(BuLi)_6$. The monomer form lies in equilibrium with hexamer form, and it is the former one that actually initiates polymerization. The research work carried out by Sinn and Onsager,[16] which shows decreasing order of reaction with respect to Li-catalyst if its concentration is increased, affords another instance in support of the tendency of organolithium compounds to associate. They used lithium polyisoprenyl as catalyst made from *n*-butyllithium and isoprene. If one compares Arrhenius reaction constants E_a and A of the systems PhOLi/PO/PhOH and PhONa/PO/PhOH, one notices an extraordinarily abrupt difference between the two sets

	E_a, kcal/mol	A, sec^{-1}	$\Delta S^{\neq}$, cal/mol deg
PhOLi	10.6	8.97×10^2	-39.3
PhONa	14.4	5.2×10^6	-28.0

A lower value of apparent activation energy in

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* See also ref 10.

the case of PhOLi should, according to the Arrhenius equation

$$k = A \exp(-E_a/RT)$$

result in a higher value of rate constant. Actually, there is no corresponding rise in k. A decrease in the value of E_a is accompanied by decrease in A, which keeps k low for PhOLi. This phenomenon, which is termed as compensation effect, is observed for PhOLi in the system phenol—ethylene oxide in homogeneous phase.[17]

EXPERIMENTAL

Materials

The chemicals used for this study, after appropriate purification, were as follows

Monomer: propylene oxide (Farbwerke, Hoechst, polymerization grade)

To remove last traces of acetaldehyde-impurity from propylene oxide, the epoxide was prepolymerized with an alkali phenoxide and phenol in the ratio of approximately 200 : 10 : 1 in a big glass-ampoule.

Catalyst: lithium phenoxide (prepared and purified in the laboratory).

Proton-active agent: phenol (Merck, distilled and purified in the laboratory)

Methods and Equipment

The classical ampoule method was employed to obtain concentration—time curves. Reaction solution of phenol, propylene oxide, and lithium phenoxide was prepared by putting a definite amount of catalyst lithium phenoxide to a weighed quantity of phenol; to this mixture was added a measured volume of propylene oxide with the help of a thermostated burette. This reaction solution was sucked in an injection (thermostated) glass tube from which a small dose (0.3—1.5 ml) of the solution was transferred in different ampoules, which were sealed by cool-and-thaw method in a high vacuum apparatus. The sealed ampoules were allowed to react at certain temperatures in a water-thermostat before they were opened for analysis. Since the reaction under study is very sensitive to air and moisture, the experiments were strictly carried out in an inert atmosphere of catalytically purified N_2 and under high vacuum.

Analysis

Concentration—time curves were based on the conversion of phenol after reaction—concentrations in moles per litre at zero time were known since a weighed amount of phenol was always taken, and the rest of the phenol was determined by analysis of the reaction mixture. For titration of phenol the quarternary tert-butyl ammonium hydroxide was used as a neutralizing solution.

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