716. *The Reaction between Phenol and Ethylene Oxide.*

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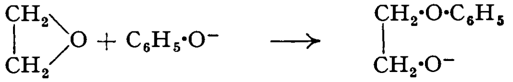
Ethylene oxide has been treated with phenol in glass apparatus at super-atmospheric pressure at 190—210° in the presence of a little sodium phenoxide. The reaction proceeds completely preferentially as far as phenoxyethanol, but thereafter mixtures of the monophenyl ethers of polyoxyethylene glycols are formed, and the amount of the individual ethers in the mixture, at least as far as the fifth member, closely followed a distribution of the Poisson series type. The distribution can be calculated on the basis that each step in the building up of the polyoxyethylene chain is identical in nature. The preferential formation of the first member of the ether series has also been shown to apply to alkylated phenols.

The reaction between phenol and ethylene oxide was shown by Boyd and Marle (*J.*, 1914, **105**, 2117) to proceed much more rapidly in the presence of an alkali, and they studied the kinetics of the reaction of phenol with one molar equivalent of ethylene oxide in alcoholic solution at 50—100°, showing that reaction takes place *via* the phenoxy-ion, as follows :



Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 994) described the reaction of equimolar quantities of phenol and ethylene oxide in an autoclave, charged with hydrogen under pressure and heated to 200° for four hours, a 94% yield of phenoxyethanol being obtained. The same reaction has also been carried out with sulphuric acid as a catalyst (Fourneau and Ribas, *Bull. Soc. chim.*, 1926, **39**, 1584; Smith and Niederl, *J. Amer. Chem. Soc.*, 1931, **53**, 806). The mechanism of the reaction in this case is stated to be *via* the intermediate formation of hydroxyethyl hydrogen sulphate, $OH\cdot CH_2\cdot CH_2\cdot SO_4H$. The reaction of ethylene oxide with alkylphenols to give alkylphenoxyethanols is described by Rohm and Haas (U.S.P. 2,075,018; B.P. 463,991). The reaction is carried out with powdered sodium hydroxide as catalyst in dry ethanol, first at 10—15°, then at 50—55°, and finally at 80—82°, the yield being 91%. The condensation of alkylphenols with several molar equivalents of ethylene oxide is described in a number of patent specifications and reports on German industry (*e.g.*, B.P. 452,866, 470,181, 479,899, 487,669, all to I.G. Farbenind.; B.P. 594,475—9, to Rohm and Haas; U.S.P. 2,158,957/8 to Dow Chem. Co.; B.I.O.S. Final Reports Nos. 418 and 1483 and Misc. Report No. 11; F.I.A.T. Final Report No. 1141).

The reactions are normally carried out at 210°, sodium hydroxide being used as catalyst, and ethylene oxide injected under pressure into the reaction mixture.

The products obtained in such reactions consist of mixtures of phenyl ethers of polyoxyethylene glycols, which can be formulated as $Ph{\cdot}O{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_{n-1}{\cdot}CH_2{\cdot}OH$, where n is the number of ethylene oxide units condensed on to the phenol, and is commonly defined as "the ethylene oxide chain length" of the "polyglycol ether." Studies of the distribution of products of various chain lengths in the mixture have not been described in the literature, either on a theoretical or on an experimental basis, but the case of the condensation of ethylene oxide with glycol (or water) has been considered theoretically by Flory (*J. Amer. Chem. Soc.*, 1940, **62**, 1561), who showed that Poisson's distribution should apply. No experimental confirmation has been published, but this conclusion has been used to predict the composition of the commercial product "Polyglycol 400" (Carbide and Carbon Chemicals Corp., "Carbowax Compounds and Polyethylene Glycols," 1946).

Ethylene oxide condensations proceed exclusively by the addition of single units of "monomer" (*i.e.*, ethylene oxide) to molecules possessing the propagating functional group (usually OH, but also SH, or NH). Thus, if the initial species is m_1, and bears the propagating functional group, m is ethylene oxide, and m_x is the product formed from m_1 and $(x - 1)$ ethylene oxide molecules, the polymerisation can be indicated as follows:

$$m_1 \xrightarrow{+m} m_2 \xrightarrow{+m} m_3 \text{ etc.} \longrightarrow m_x$$

Reaction of the type $m_x + m_y \longrightarrow m_{x+y}$ does not occur. This is in direct contrast to the case of condensation polymerisation, where this reaction does take place, x and y being integers of any size from 1 to infinity. It has been demonstrated in the case of polyesterification that all these reactions proceed with equal ease (*idem, ibid.*, 1939, **61**, 3334).

Mark ("The Chemistry of Large Molecules") has stated that "It is not known to what extent the collision factor and the activation energy of the reaction step depend upon the chain length of the alcohol, but by analogy with the polycondensation processes one would be induced to conclude that it depends but little."

Flory's derivation of the distribution of chain lengths can be simplified as follows. It is based on the following two assumptions: (*a*) That the total number of molecules possessing the propagating functional group remains constant, *i.e.*, that each addition of monomer regenerates such a group. (*b*) That the chains are built up by a sequence of kinetically identical steps.

If n_x is the number of molecules at any time t of the species m_x, then

$$dn_1/dt = -fn_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f is a factor depending upon the kinetics of the process, and the manner in which it is performed; f will be a function of the velocity constant, the concentration of ethylene oxide, time, and the total number of propagating molecules N $(= \Sigma n_x)$. In view of assumption (*b*), the rate at which m_2 is converted into m_3 at the same instant will similarly be fn_2.

Hence

$$dn_2/dt = fn_1 - fn_2$$

and

$$dn_x/dt = fn_{x-1} - fn_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If m is the number of molecules of ethylene oxide present, then, since the consumption of ethylene oxide proceeds at a rate equal to the total reaction rates of the propagating molecules:

$$dm/dt = -fN \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

i.e.,

$$-\int_{m_0}^{m_t} dm = N\int_0^t f\,.\,dt$$

If v is the mean chain length at time t, v is the ratio of ethylene oxide consumed at time t to the total number of propagating molecules, *i.e.*,

$$v = (m_0 - m_t)/N = \int_0^t f\,.\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting for f from (4) in (1) and (2), we have

$$\mathrm{d}n_1 = -n_1 \,.\, \mathrm{d}v \qquad (5)$$

and

$$\mathrm{d}n_x = (n_{x-1} - n_x)\mathrm{d}v \qquad (6)$$

From (5)

$$\int_N^{n_1} \frac{\mathrm{d}n_1}{n_1} = -\int_0^v \mathrm{d}v$$

whence

$$\log n_1/N = -v \text{ and } n_1 = N\mathrm{e}^{-v}$$

Insertion of this value for n_1 in equation (6) when $x = 2$, and integration of the resulting equation gives $n_2 = Nv\mathrm{e}^{-v}$; similarly for $x = 3$, $n_3 = (Nv^2/2!)\mathrm{e}^{-v}$, and continuation of the same process gives the general solution :

$$n_x = N\frac{v^{x-1}}{(x-1)!}\mathrm{e}^{-v} \qquad (7)$$

Equation (7) is thus a general expression for mole-fraction distribution. It can be modified into terms of weight-fraction distribution, as follows :

If M is the molecular weight of the initial material, M_x that of a product of chain length x units, and W_x is the weight-fraction of product of chain length x units, then 44 being the molecular weight of ethylene oxide, we have

$$W_x = M_x n_x/\Sigma M_x n_x = M_x n_x/(M + 44v)N$$

$$= \frac{M_x}{M + 44v}\,.\,\frac{v^{x-1}}{(x-1)!}\mathrm{e}^{-v} \qquad (8)$$

The present investigation was concerned with testing the applicability of equation (8) to the reaction products between phenol and ethylene oxide.

The procedure adopted was to treat phenol (or one of the lower ethers) with ethylene oxide at 190—210° and a super-atmospheric pressure of about 600 mm. in the presence of 0·05 equiv. (on the phenol or ether) of sodium or sodium hydroxide. The reaction product was then neutralised with sulphuric acid, and fractionally distilled. The fractions of constant boiling point were identified by their boiling point and refractive index; the intermediate fractions were analysed by determining their refractive index, and direct interpolation from calibration curves, constructed from known mixtures, which were prepared once samples of the known individuals were to hand. Fairly pure samples of the monophenyl ethers of the polyoxyethylene glycols up to the fifth member in the series were obtained during the course of the work, and these were redistilled until pure specimens were obtained for the purpose of constructing the calibration curves referred to above.

The condensation of the first molecule of ethylene oxide with phenol was examined first by using one equivalent of ethylene oxide or less. It was found in all these cases that continued distillation of the product of reaction gave no material of higher boiling point than phenoxyethanol. The results of four experiments are shown in the following table, and the amount of unchanged phenol in the product is calculated on the basis that all the ethylene oxide is consumed solely by reaction to give phenoxyethanol. When sodium hydroxide was used as catalyst, but not when sodium was used, traces of ethylene glycol were also formed. This accounts for the better agreement between found and calculated values for unchanged phenol in the latter experiment.

Reaction of phenol with 1 *mol. or less of ethylene oxide.*

Expt. No.	Catalyst.		C_2H_4O/C_6H_6O, molar.	Condn. rate : mols. C_2H_4O/mol./hr.	Unchanged phenol.	
	Type.	Mol.-%.			Found, %.	Calc., %.
0/3	NaOH	4·7	1·08	0·62	1	0
0/4	NaOH	4·7	0·835	1·4	14·6	11·7
0/5	Na	1·1	0·755	0·62	19·3	18·0
0/6	Na	0·54	0·944	0·81	3·7	3·9

Phenoxyethanol was then condensed with just less than its equivalent of ethylene oxide. In these cases it was found that the products consisted of a mixture of ethers, and the weight distribution was calculated from equation (8), by substituting $M = 138$, the molecular weight of phenoxyethanol, and $v = 0{\cdot}905$, the molar ratio of ethylene oxide to phenoxyethanol used. The results were as follows :

Production of ethers, $Ph{\cdot}O{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_{n-1}{\cdot}CH_2{\cdot}OH$, *from phenoxyethanol.*

Expt. No.	1/2.	1/3.	1/4.	Calc.
Catalyst, nature	NaOH	Na	Na	—
Catalyst, mol. %	1·17	1·02	0·50	—
C_2H_4O/Phenoxyethanol, molar	0·905	0·905	0·905	—
Condn. rate, mols. C_2H_4O/mol./hr.	1·5	1·0	2·4	—
Product analysis :				
$n = 1$, %	29·4	30·2	28·8	31·3
$n = 2$, %	44·3	—	—	37·5
$n > 2$, %	26·3	—	—	31·2

Further studies were carried out with a variety of initial ethers, the product being examined in each case for one or two main constituents. The calculation of results was based on the supposition that, starting with phenol itself, the first molecule of ethylene oxide reacts completely preferentially with the phenol, but that thereafter the conditions which form the basis for the derivation of equation (8) apply, *i.e.*, that the chains are built up by a sequence of kinetically identical steps, each addition of monomer regenerating the functional hydroxyl group. The results are given below ; in three cases, pairs of products were combined for fractionation.

Condensation of ethylene oxide with monophenyl ethers of polyoxyethylene glycols.

Expt. no.	Reactant, *n*.	C_2H_4O, mols.	Na, mols. %.	Cond. rate, mols. C_2H_4O/mol./hr.	Product analysis : *n*.	Found, %.	Calc., %.
0/7	0	2·95	1·09	2·36	0 1	0 5·3	0 8·8
0/8	0	1·01	0·55	0·87	0	2·2	0
0/9	0	1·80	1·16	1·22	1	35·9	36
0/10	0	1·76	1·16	1·3	1	35·7	36·3
1/8	1	0·82	1·45	1·23			
1/5	1	1·97	1·09	2·23	1	3·2	8·5
1/6	1	0·81	1·45	1·6	1	34·3	35·4
1/7	1	0·81	1·45	1·2	2	42·3	37·8
1/9	1	0·83	1·45	1·08	1	15·0	15·5
2/2	2	0·85	1·45	1·13	2	37·2	36·5
2/1	2	0·82	1·45	1·8	2	38·7	36·6
2/3	2	0·84	1·45	1·69	2	35·8	35·8
3/1	3	0·86	1·43	3·44	—	—	—

In a further experiment phenol was treated with a larger amount of ethylene oxide, and the product obtained analysed the more fully. The calculated distribution given below assumes as before that no condensation of ethylene oxide with an ether occurs until the phenol is completely converted into the first member, and that thereafter all the ethers compete for ethylene oxide on equal terms.

Condensation of 3·43 *moles of ethylene oxide with phenol. Weight distribution of* $Ph{\cdot}O{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_{n-1}{\cdot}CH_2{\cdot}OH$.

n	1	2	3	4	>4
Found, %	4·7	17·8	27·1	21·1	29·3
Calc., %	4·9	15·9	24·0	23·2	32·0

It was not possible to carry out parallel work with alkylated phenols, as the separation of the various ethers in each case by fractional distillation becomes difficult. It was possible, however, to test whether formation of the first member of the ether series is completely preferential. This was done by using just less than the equivalent amount of ethylene oxide, and examining the amount of unchanged alkylphenol in the product. The results were as follows :

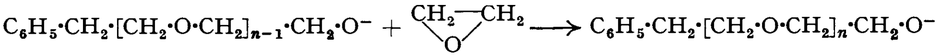
Condensation of ethylene oxide with alkylphenols.

Alkylphenol.	C_2H_4O, mols.	Na, mols. %.	Condn. rate, mols. C_2H_4O/mol.hr.	Unchanged alkylphenol. Found, %.	Calc., %.
o-Cresol	0·86	1·45	1·15	10·7	10·2
p-1 : 1 : 3 : 3-Tetramethylbutylphenol	0·975	1·47	3·1	None	2·1
5-1′ : 1′ : 3′ : 3′-Tetramethylbutyl-*o*-cresol	0·756	1·45	1·46	23	21

Following the reaction mechanism of Boyd and Marle (*loc. cit.*), with which the above results are in agreement, the first stage in the reaction of ethylene oxide with phenol in presence of alkaline catalysts is to form the ion of phenoxyethanol (see p. 3623). So long as any unreacted phenol is present, the next step must be proton transfer between this ion and the phenol molecule :

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O^- + C_6H_5{\cdot}OH \longrightarrow C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}O^-$$

When all of the phenol present has reacted, the alkoxyl ion then proceeds to react, and form the ion of the next member in the series of ethers. Since this does not initiate a chain reaction, it must be followed by interaction of the ion with an un-ionised molecule of hydroxy-ether, not necessarily of the same chain length. Thus



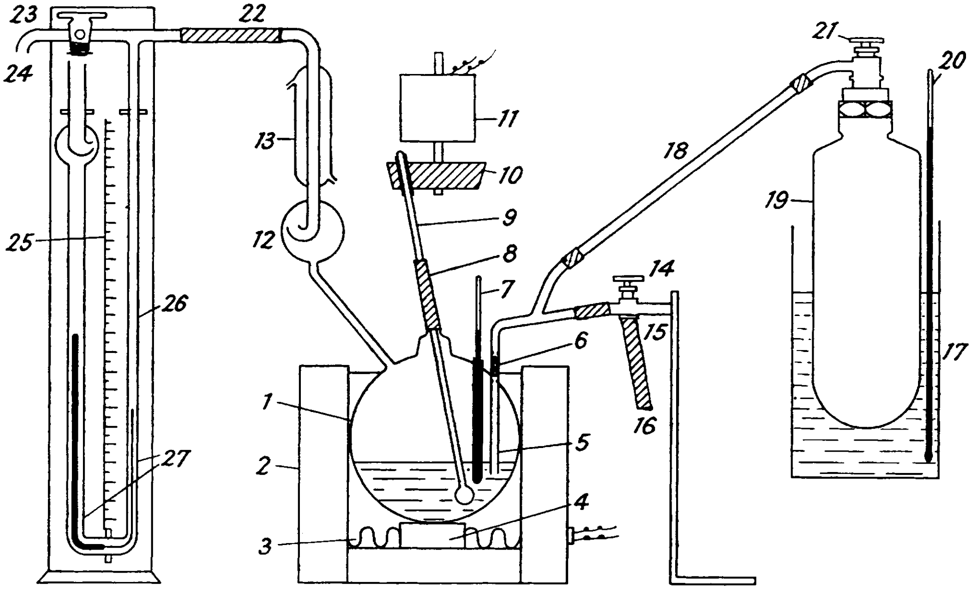
$$C_6H_5{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_{n-1}{\cdot}CH_2{\cdot}O^- + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow C_6H_5{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_n{\cdot}CH_2{\cdot}O^-$$

$$C_6H_5{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_n{\cdot}CH_2{\cdot}O^- + C_6H_5{\cdot}O{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_x{\cdot}CH_2{\cdot}OH \longrightarrow$$
$$C_6H_5{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_n{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}O{\cdot}CH_2{\cdot}[CH_2{\cdot}O{\cdot}CH_2]_x{\cdot}CH{\cdot}{}_2O^-$$

The latter reaction can be brought about by any un-ionised molecule, and the value of x is determined in any individual case by the laws of probability, and thus depends on the mole-fraction of any given polymer present at the time. In other words, once the phenol has reacted completely, all the hydroxyl groups are equivalent, irrespective of the length of the oxyethylene chain separating them from the aromatic nucleus.

EXPERIMENTAL.

The apparatus used to carry out the reactions at super-atmospheric pressure is shown diagrammatically in the accompanying figure, which is largely self-explanatory; the temperature of the ethylene oxide cylinder was kept at 30—40°, the reaction flask was of 500 ml. capacity, and the limiting pressure was 760 mm. above atmospheric.



1. *Reaction flask.*
2. *Asbestos air bath.*
3. *Nichrome wire heating coil.*
4. *Asbestos block.*
5. *Inlet tube for nitrogen.*
6. *Non-return valve.*
7. *Thermometer* 0—250°.
8. *Flexible rubber gland wired on.*
9. *Paddle stirrer.*
10. *Eccentrically bored rubber bung.*
11. *Electric motor.*
12. *Splash head.*
13. *Condenser.*
14. *Needle valve for* N_2 *control.*
15. ⅜ *in. I.D. pressure tubing.*
16. *Nitrogen inlet.*
17. *Water bath.*
18. ¼ *in. Glass tubing.*
19. *Steel cylinder for ethylene oxide.*
20. *Water bath thermometer.*
21. *Needle valve for ethylene oxide control.*
22. ¼ *in. I.D. pressure tubing.*
23. *Spring loaded stopcock.*
24. *Exit for purge gases.*
25. *Meter scale.*
26. *Capillary tubing.*
27. *Mercury gauge.*

The reaction vessel was heated electrically. On the scale used it was not necessary to cool the reactor artificially when the reaction was in progress, the voltage supplied to the electric heater being controlled by a Variac transformer. All the junctions on the ethylene oxide inlet side of the apparatus were made as glass-to-glass butt joints, the rubber tubing serving only as a seal, and the leads were lifted at an oblique angle to the apparatus, to prevent any contamination of the feed from the rubber tubing (in which the ethylene oxide might otherwise condense as liquid). All the rubber junctons were wired.

In a typical run, 188 g. of phenol were charged into the reactor, and the air in the apparatus displaced with nitrogen. Freshly cut metallic sodium (0·25 g.) was added, the stirrer attached, and the sodium dissolved on warming to about 80°, still in a current of nitrogen. The mixture was then heated to 160°, ethylene oxide passed in to displace the nitrogen, the system then closed, and the feed adjusted so as to maintain a pressure of 600 mm., with a reaction temperature of 190—210°. The requisite amount of ethylene oxide having previously been weighed into the feed cylinder, the reaction was complete when it was no longer possible to raise the pressure in the system even by opening the cylinder valve fully. The reaction product was neutralised by the addition of 50% sulphuric acid equivalent to the sodium taken, and then fractionally distilled through a column packed with Fenske glass helices, equivalent to 14 theoretical plates.

The purified phenyl ethers isolated are tabulated below.

Monophenyl ethers of polyoxyethylene glycols, $Ph\cdot O\cdot CH_2\cdot[CH_2\cdot O\cdot CH_2]_{n-1}\cdot CH_2\cdot OH$.

n.	1.	2.	3.	4.	5.
B. p./mm.	120·5°/9	163·0°/8	190·5°/8	181°/0·2	218°/0·4
n_D^{20}	1·5370	1·5230	1·5144	1·5075	1·5030
d_4^{20}	1·108	1·115	1·120	1·121	1·121
Found, C, %	69·3	66·0	63·4	61·8	61·1
„ H, %	7·4	8·0	8·4	8·3	8·6
„ *M*	—	193	230	269	324
Calc., C, %	69·5	65·9	63·7	62·2	61·1
„ H, %	7·3	7·7	8·0	8·2	8·3
„ *M*	—	182	226	270	314
In water	Insol.	—	Sol.	Sol.	Sol.

The second member of the series and water emulsified when shaken. The molecular weights were determined ebullioscopically in benzene.

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