

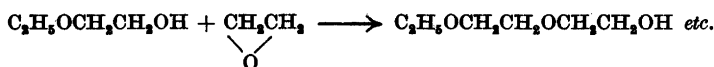
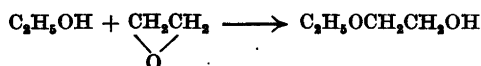
The Distribution of Compounds Formed in the Reaction between Ethylene Oxide and Water, Ethanol, Ethylene Glycol, or Ethylene Glycol Monoethyl Ether*

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Addition of ethylene oxide to compounds containing an active hydrogen atom leads to a series of consecutive reactions. A theory is developed for the distribution of the compounds formed. The assumption is made that all steps except the first one are kinetically identical. It is shown that the distribution is determined by the proportion between the starting materials and by the ratio of the identical rates of the higher steps to the rate of the first one. The theory is tested by experiment and also by recalculation of previously published data. The agreement is satisfactory.

Compounds containing an active hydrogen atom react with ethylene oxide to give a series of consecutive, irreversible, competitive reactions, in which a reactive hydroxyl group is formed in every step. With ethanol, for instance, the reactions are:



From both theoretical and technical points of view it is important to know the distribution of compounds obtained under various conditions. Before this problem is considered, a few words must be said concerning the molecular mechanism of the reaction. Ingold¹ recently gave a survey of this question. It seems to be agreed that the reaction is a nucleophilic substitution by means of the reactive group on a carbon atom of ethylene oxide or its conjugate acid.

* Part of this work was presented at the XIIIth International Congress of Pure and Applied Chemistry, Stockholm 1953.

Under acid or neutral conditions the nucleophilic reagent in the example cited above is the undissociated alcohol, but under alkaline conditions the reagent is the corresponding base, *i.e.* the alcoholate ion. The various mechanisms will affect the distribution of the products formed. The simple, uncatalysed reaction will first be considered, and the treatment will then be modified for the catalysed reactions.

Flory² in 1940 calculated the distribution of products in the reaction of ethylene oxide with a compound with a reactive group. He made the assumption, that all steps in the reaction sequence are kinetically identical and showed that a Poisson distribution results.

Natta *et al.*³⁻⁵ considered the distribution of products in a series of consecutive competitive reactions where the various steps proceed with different rates. He arrived at formulae in which the concentrations of the various products were obtained as functions of the concentration of the remaining, unchanged starting material. In principle the same formulae were derived as early as 1906 by Abel⁶ who considered the stepwise saponification of esters of polyvalent alcohols. Martin and Fuchs⁷ obtained the same formulae for the case of the stepwise chlorination of alkanes.

All of these authors, except Flory, derived their expressions assuming second order kinetics and a constant volume throughout the reaction. Fuoss⁸ discussed four consecutive reactions and adopted a method using reaction probabilities for the derivation of the distribution of compounds. His results were identical with those obtained by the kinetic method, as pointed out by Potter and Macdonald⁹.

The assumption of Flory that all steps are kinetically identical is, in most cases, an over-simplification. On the other hand the formulae of Natta are very cumbersome, so it seemed justified to find a reasonable approximation. As is seen from the reaction scheme the reactive hydroxyl group is bound to an oxyethylene group in every step except the first one. It therefore seemed chemically justified to assume that all steps except the first one proceed with equal rate.

In the technical manufacture of glycol products, ethylene oxide is generally added continuously to the well-mixed, liquid batch, and this is also the practice in laboratory experiments. For the derivation of equations it was therefore considered justified, not to use the common kinetic arguments, but rather a probability method similar to that used by Fuoss. It is assumed that the mixing is ideal, so that concentration gradients do not occur. We first derive general equations and then introduce the appropriate simplifications. The following notation is used:

N_i	molecule with i added ethylene oxide molecules
m	number of moles of ethylene oxide
n_{00}	» » » » starting material
n_i	» » » » N_i in the reaction product
k_i	velocity constant for the reaction of N_i with ethylene oxide
c_i	= k_i/k_0 named distribution constant as proposed by Natta ⁵
v	= m/n_{00} average number of moles of ethylene oxide per mole of starting material

If the hydroxyl groups of all the reacting species are equally reactive, the reaction probability of each species is equal to its mole fraction. If dm moles of ethylene oxide react, the amount reacting with species N_i thus equals $dm \frac{n_i}{\sum n_j}$. If the reactivities are not equal, the reaction probabilities are proportional to the velocity constants. We then get, for the amount reacting with species N_i , the analogous expression $dm \frac{k_i n_i}{\sum k_j n_j}$. We thus obtain the following system of differential equations:

$$\frac{dn_0}{dm} = - \frac{k_0 n_0}{\sum k_j n_j} \quad (1)$$

$$\frac{dn_i}{dm} = \frac{k_{i-1} n_{i-1}}{\sum k_j n_j} - \frac{k_i n_i}{\sum k_j n_j} \quad (2)$$

$$\sum n_j = n_{00} \quad (3)$$

$$v = \frac{m}{n_{00}} \quad (4)$$

Equation (1) gives the decrease of the starting material and equation (2) the increase of the compounds formed. Equation (3) expresses the fact that the number of reacting molecules is constant throughout the reaction. Equation (4) defines v . Dividing equation (2) by equation (1):

$$\frac{dn_i}{dn_0} = \frac{c_i n_i - c_{i-1} n_{i-1}}{n_0} \quad (5)$$

This can be evaluated to the recursion formula (6) which gives n_i as a function of n_{i-1} and n_0 :

$$n_i = c_{i-1} n_0 \int_{n_0}^{n_{i-1}} \frac{1}{n} e^{-c_{i-1} n} dn \quad (6)$$

Solution of this integral leads to different results dependent upon the values of the distribution constants c_i . If all reactive groups are equally reactive, all c_i are equal to unity. Using equation (4) we obtain Flory's formula:

$$\frac{n_i}{n_{00}} = e^{-v} \frac{v^i}{i!} \quad (7)$$

If all reactive groups have different reactivities, all c_i are different and we obtain a formula equivalent to that of Natta:

$$\frac{n_i}{n_{00}} = (-1)^i \prod_{j=1}^{i-1} c_j \sum_{j=0}^i \frac{1}{\prod_{\substack{k=0 \\ k \neq j}}^i (c_j - c_k)} \left(\frac{n_0}{n_{00}} \right)^{c_j} \quad (8)$$

Finally, if we assume that all hydroxyl groups bound to an oxyethylene group have identical reactivity, which differs from that of the reactive group of the starting material, all distribution constants are equal ($= c$) but different from unity. Keeping in mind that $\sum c_j n_j$ then equals $n_0 + c(n_{00} - n_0)$ we obtain, by integrating equation (1) and using equation (6), the following expressions:

$$v = c \ln \frac{n_{00}}{n_0} - (c-1) \left(1 - \frac{n_0}{n_{00}}\right) \quad (9)$$

$$\frac{n_i}{n_{00}} = \frac{c^{i-1}}{(c-1)^i} \left\{ \frac{n_0}{n_{00}} - \left(\frac{n_0}{n_{00}}\right)^c \sum_{j=0}^{i-1} \frac{1}{j!} \left[(c-1) \ln \frac{n_{00}}{n_0} \right]^j \right\} \quad (10)$$

Equation (9) gives the interdependence of n_0/n_{00} , c , and v . It is seen, that it is not possible to obtain n_0/n_{00} as an explicit function of v and c . Equation (10) gives n_i/n_{00} as a function of the concentration of the unchanged starting material, n_0/n_{00} , with c as a parameter. These formulae are somewhat complicated to use, but much easier to handle than formula (8). Their usefulness will be tested in the experimental part.

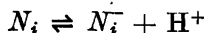
During the preparation of this paper a preliminary communication by Gold¹⁰ came to our notice. This author presents, in a different form, the same formulae as our equations (9) and (10), but no derivation is given.

Till now we have assumed uncatalysed conditions. In the case of acid catalysis exactly the same reasoning may be applied leading to identical equations. Generally the values of the distribution constants c_i change, as the reactivities of the reactive groups towards the conjugate acid of ethylene oxide may be different from those towards the neutral oxide.

In the case of alkaline catalysis the equations must be modified. It is assumed that we may disregard the reaction of the undissociated molecules in comparison with the corresponding anions. In that case we can apply the same reasoning as above to the anions and get:

$$\frac{dn_i}{dm} = \frac{\bar{k}_{i-1} \bar{n}_{i-1}}{\sum \bar{k}_j \bar{n}_j} - \frac{\bar{k}_i \bar{n}_i}{\sum \bar{k}_j \bar{n}_j} = \frac{\bar{c}_{i-1} \bar{n}_{i-1}}{\sum \bar{c}_j \bar{n}_j} - \frac{\bar{c}_i \bar{n}_i}{\sum \bar{c}_j \bar{n}_j} \quad (11)$$

where \bar{n}_i is the number of moles of N_i^- , the anion corresponding to N_i and $\bar{c}_i = \bar{k}_i/\bar{k}_0$. The velocity constants \bar{k}_i refer to the reactions of the anions with ethylene oxide. In order to determine \bar{n}_i we study the protolytic equilibrium of the reactive molecules, which may be put thus:



If the equilibrium constant is K_i , the concentration of H^+ is h , and the concentration of the catalyst is a , we have:

$$\frac{\bar{n}_i \cdot h}{\bar{n}_i - \bar{n}_i^-} = K_i \quad (12)$$

$$\sum \bar{n}_j = a \quad (13)$$

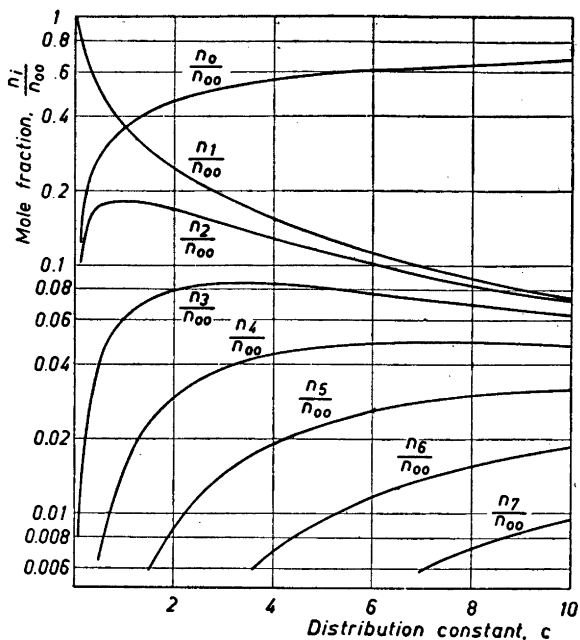


Fig. 1. Distribution of compounds formed by the addition of one mole of ethylene oxide to one mole of reactive substance; n_i/n_{00} = mole fraction of compound with i moles of ethylene oxide added; c = distribution constant.

n_i^- may be neglected in comparison with n_i and we get:

$$n_i^- = a \frac{K_i n_i}{\sum K_j n_j} = a \frac{c'_i n_i}{\sum c'_j n_j}, \text{ where } c'_i = K_i/K_0 \quad (14)$$

When substituting the value of n_i^- from (14) in (11), this equation takes the same form as equation (2) and may be solved in the same way. We obtain solutions corresponding to equations (8) to (10), where the products $c_i^- c'_i$ are substituted for the constants c_i . Here c_i^- is a measure of the reactivity of the anions towards ethylene oxide and c'_i a measure of the acidity of the hydroxyl groups in comparison with the corresponding properties of the starting material.

Thus it is seen that equations of the form (8) to (10) account for the distribution of compounds formed in the reaction of ethylene oxide with substances with an active hydrogen atom, with or without acid or alkaline catalysts. Fig. 1 gives a graphical representation of the equations (9) and (10) for various values of c with $v = 1$, i.e. equimolecular amounts of starting material and ethylene oxide.

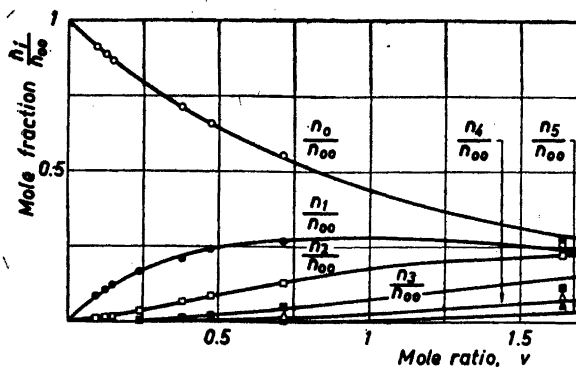


Fig. 2. Distribution of compounds formed by the addition of ethylene oxide to water with sulphuric acid as catalyst; n_i/n_{00} has the same meaning as in Fig. 1; v = mole ratio of reactants, ethylene oxide / water.

EXPERIMENTAL VERIFICATION

Previous work

Only a few papers have been published concerning the reaction of ethylene oxide with reactive molecules, where the reaction product was analysed with sufficient accuracy to be of value for the testing of the formulae given above.

Matignon, Moureu, and Dodé¹¹ studied the hydration of ethylene oxide with sulphuric acid as catalyst. They analysed the reaction product by distillation and the composition of the fractions by measuring their refractive indices. The percentages of ethylene oxide used up for the formation of the various compounds were reported. The amount of unchanged starting material (*i. e.* water) was not determined, but can be calculated by difference. In Fig. 2 the points correspond to the experimental data, corrected for losses during the analyses (5%). The curves are calculated with equations (9) and (10) on the assumption that $c = 1.66$. The curves fit the points fairly well.

Recently the hydration of ethylene oxide was experimentally studied also by Davis, von Waaden, and Kurata¹². As their paper reached us only when our paper was ready for publication, comparison between our formulae and their results is not made. However, qualitative agreement at least seems to exist between their work and ours.

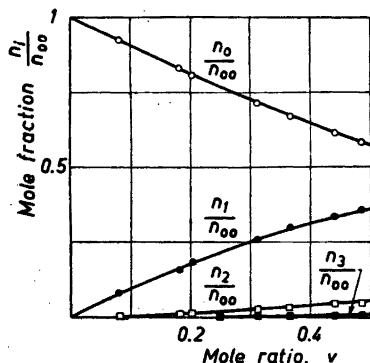


Fig. 3. Distribution of compounds formed by the addition of ethylene oxide to methanol; n_i/n_{00} and v have the same meaning as in previous Figures.

Natta and Simonetta⁴ gave results for the reaction between ethylene oxide and methanol or monomethyl ethers of ethylene glycol and diethylene glycol. The reactions were carried out in an autoclave at various temperatures without added catalysts. The analyses of the products were made as in the work by Matignon, Moureu, and Dodé but no details were given. In the case of the glycol ethers most of the ethylene oxide used remained unreacted, so the yields of the reaction products were low and seem uncertain. These results are therefore not used to test our equations. The data concerning the reaction between methanol and ethylene oxide are treated as above and the results are plotted in Fig. 3. The effect of the temperature variations has not been considered. The theoretical curves are calculated on the assumption that $c = 0.55$. The agreement between experiment and theory seems good in this case too.

The reaction between ethylene oxide and phenol with an alkaline catalyst was studied by Miller, Bann, and Thrower¹³ and by Patat, Cremer, and Bobleter¹⁴. Both groups of investigators found that the monophenyl ether of ethylene glycol is exclusively formed before the ethylene oxide reacts with the glycol hydroxyl group. Then a mixture of the monophenyl ethers of polyoxyethylene glycols results which, according to the former group of authors, has a distribution of the Poisson-series type. In the papers mentioned it is assumed that the preferential formation of the first member of the product series is caused by phenol being more acidic than the various glycol ethers. The latter may all be considered equally acid and therefore the distribution constants c'_i in equation (14) are equal and very small, thus giving also to the constant c of equations (9) and (10) a low value. It is easily seen from the equations and also from Fig. 1 that, for $v = 1$ and c approaching 0, n_0/n_{00} also approaches 0 and n_1/n_{00} approaches unity. The phenyl ether of glycol is thus preferentially formed and acts as starting material when further amounts of ethylene oxide are added. The compounds formed are distributed according to a Poisson series as their reactivities are equal to that of the glycol ether.

Present work

Procedure. Experiments were carried out on the reaction between ethylene oxide on the one hand and water, ethylene glycol (henceforth simply named glycol), ethanol, or monoethylether of ethylene glycol (henceforth ethylglycol) on the other. With water, experiments were made without catalyst and also with oxalic acid, carbonic acid, sodium carbonate, or sodium hydroxide as catalyst. In the experiments with the alcohols the corresponding sodium alcoholates were the catalysts. The experiments with water without catalyst and with carbonic acid as catalyst were carried out in a 2 litre autoclave equipped with stirrer and kept at the desired temperature by means of circulating oil. The ethylene oxide was charged in portions from a steel container and introduced into the autoclave by heating the container in a water bath. The ethylene oxide could not be charged in one portion as this would lead to excessive pressure and temperature. All the other experiments were carried out in a glass apparatus at atmospheric pressure. The ethylene oxide was evaporated from a glass vessel and introduced at the bottom of the reaction vessel by means of a glass filter. The liquid material was stirred by the gas bubbles and kept at constant temperature by means of a regulated bath. The reaction vessel was also equipped with a reflux condenser, cooled to -15°C to prevent evaporation. The amount of starting material was accurately weighed at the beginning of the experiment and the amount of ethylene oxide reacted was determined as the increase in weight, at the end of the experiment. The experimental errors in these experiments were smaller than those of the autoclave runs.

Equimolecular amounts of the reaction components ($v = 1$) were used in most cases, but in some cases this led to such large amounts of the higher products that it was found impossible to separate the components. In these cases a lower proportion of ethylene oxide was used. The analysis of the reaction product was carried out by distillation. Each fraction contained at most two components. Their proportions were calculated from the hydroxyl content, determined by acetylation, and in some cases also from water analyses according to Fischer, and ethylene glycol analyses by periodate oxidation. Where equimolecular amounts of the reaction components were used the fractionations were made directly on a 40 ml sample of the product in a spinning band column according

Table 1. Reaction between ethylene oxide and various substances. Experimental conditions, and experimental and theoretical distribution of compounds in reaction product.

1	2	3	4	5		7	8	9	10	11	12	13	14	15	16	17	18	19	20
				Nature	g														
1	Water	100.00	244.75	Oxalic acid	0.30	85	1.001	E 0.460	0.262	0.163	0.075	0.028	0.016	1.003	0.990	1.95	1.85	1.9	
2	*	1 000.0	223	CO ₂	b)	105	0.0912	T 0.456	0.257	0.169	0.079	0.028	0.008	0.998	1.009	1.66	3.0	2.5	
3	*	571.0	279.5	—	—	100	0.2002	E 0.839	0.132	0.026	0.003	—	—	1.000	0.964	2.69	2.2	2.5	
4	*	1 000.0	245.85	Na ₂ CO ₃	2.65	85	0.1006	T 0.837	0.131	0.028	0.004	—	—	1.003	0.998	6.63	4.4	5.5	
5	*	1 000.2	241.3	NaOH	1.00	85 ^c	0.0986	E 0.931	0.041	0.016	0.005	0.002	—	0.997	1.015	12.0	15.5	13	
6	Glycol	150.20	106.20	Na	0.30	85	0.996	E 0.375	0.341	0.185	0.097	—	—	0.998	1.005	1.04	1.14	1	
7	Ethanol	114.5	108.8	*	1.0	65	0.994	E 0.476	0.234	0.146	0.076	0.032	0.026	0.991	1.019	2.15	2.19	2.2	
8	*	115.1	108.6	*	1.0	65	0.987	T 0.479	0.234	0.162	0.081	0.031	0.010	1.003	1.006	2.27	2.33	2.2	
9	Ethylglycol	141.23	69.65	*	0.75	65	1.009	E 0.485	0.225	0.166	0.072	0.056	—	1.010	0.991	1.06	1.03	1	
								T 0.481	0.234	0.161	0.080	0.031	—						
								E 0.372	0.362	0.187	0.088	—	—						
								T 0.365	0.368	0.186	0.062	—	—						

a) E = experimental values; T = theoretical values calculated with ν of column 8 and c of column 20.

b) The pressure of the carbon dioxide was 1 atm.

c) During the first part of the experiment the temp. was 65° C.

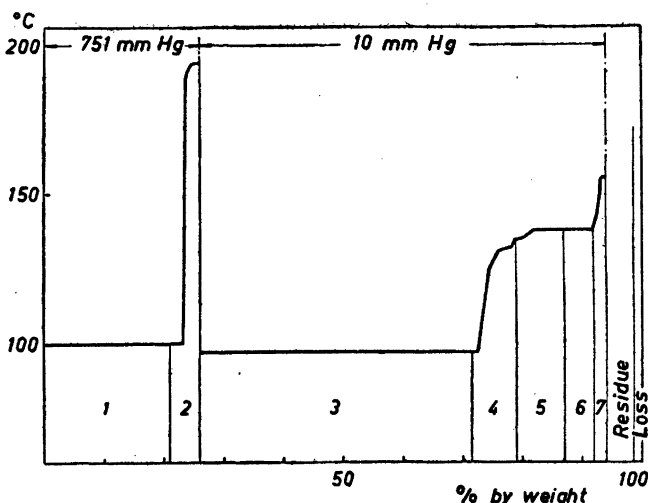


Fig. 4. Distillation curve for product obtained from reaction between ethylene oxide and water with sodium carbonate as catalyst, Experiment No. 4.

to Björkman and Olavi¹⁸. This column has about 25 theoretical plates. Where a lower proportion of ethylene oxide was used too much of the starting material remained unreacted to give accurate data for the components. In these cases most of the unchanged starting material was first distilled off in a Podbielniak "Hyper-Cal" distillation apparatus with about 50 theoretical plates and a take-off of 10 % of the total reflux. A sample of 400–500 g was used. The distillation was interrupted when the temperature in the distillation vessel was *ca.* 25° C above that of the starting material. The amount of distillate

Table 2. Analytical distillation of 43.59 g of product from the reaction between ethylene oxide and water, Experiment No. 4, Fig. 4.

Fraction No.	Amount g	% OH	Composition		Summarised composition	
			Amount, g	Compound	Compound	Amount, g
1	9.2218		9.2218	Water	Water	10.0396
2	2.1407	33.87	0.8178	»	Glycol	22.8498
			1.3229	Glycol	Diglycol	7.8040
3	19.9146		19.9146	»	Triglycol	2.2748
4	3.2664	42.60	1.5133	»		
			1.7531	Diglycol ^{a)}		
5	3.2638	32.75	0.0990	Glycol		
			3.1648	Diglycol		
6	2.1980	32.08	2.1980	»		
7	1.0229	28.98	0.6881	»		
			0.3348	Triglycol ^{b)}		
Residue	1.94	21.7	1.94	»		
Sum	42.9682					
Loss	0.62					

a) Abbreviation used for diethylene glycol.

b) » » » triethylene glycol.

was determined as loss of weight of the liquid in the distilling flask. Part of this residue was then subjected to fractionation in the spinning band column.

Materials. The organic reagents used were carefully purified. The ethylene oxide was practically free from acetaldehyde (less than 0.01 %). The ethanol was made "super dry" by distillation from a solution of magnesium ethoxide in ethanol¹⁶. The glycol and its ethyl ether were carefully fractionated in the Podbielniak distillation apparatus. The sodium alcoholate catalysts were prepared *in situ* by addition of metallic sodium to the starting materials.

Conditions and Results. The experimental conditions and results are summarised in Table 1. Before these are discussed the details of the calculations of one experiment are given as an illustration of the method used. In Experiment No. 4, 245.85 g of ethylene oxide was reacted with 1 000.0 g of water with 2.65 g of dry sodium carbonate as catalyst. The molecular proportions of the reactants, v , is calculated as 0.1006. Of the reaction product, 400.0 g was distilled in the Podbielniak apparatus giving 136.8 g of residue. Of this, a sample of 43.59 g was distilled in the spinning band column. The distillation curve is shown in Fig. 4 and the results including analyses and calculated amounts of individual compounds are given in Table 2. The residue from the distillation is counted in with the highest glycol. The amounts of water charged and distilled off in the Podbielniak apparatus are recalculated to correspond to the amount fractionated in the final distillation. In order to compensate for the distillation loss the sum of the fractions was used instead of the amount distilled. Water distilled off = $(400.0 - 136.8) (42.97/136.8) = 92.71$ g. The total amount of water in the reaction product thus was 102.75 g. Water charged = $(1\ 000.0/18.02) (400.0/1\ 248.5) (42.97/136.8) = 5.5844$ moles. The amounts of the products are converted to moles and the values of the various mole fractions n_i/n_{00} calculated (Table 1, columns 10 to 15). The sum of these mole fractions should equal unity and the sum of the expressions in_i/n_{00} should equal v . As is seen from Table 1, columns 16 and 17, the agreement is satisfactory.

The experimental results in Table 1 were obtained in the way described. Of the various values for c , c' (column 18) is calculated from v and n_0/n_{00} by means of equation (9), c'' (column 19) from n_0/n_{00} and n_1/n_{00} by iteration in equation (10), and c (column 20) is a chosen mean value. In combination with the experimental value of v (column 8), this mean value is used for the calculation of the theoretical values of n_i/n_{00} (columns 10 to 15) given below the experimental values.

It is of interest to compare the values of the distribution constants c determined by distribution experiments with those that can be calculated from determinations of the individual velocity constants. Table 3 gives velocity constants determined at 25° C on dilute solutions of ethylene oxide in the respective reagent with sodium hydroxide as catalyst¹⁷. The constants are second order constants reduced to unit molar concentration of catalyst. The quotients of the appropriate constants are compared with those determined from the distribution experiments.

Table 3. Velocity constants at 25° C and distribution constants for the reaction between ethylene oxide and various compounds with sodium hydroxide as catalyst.

Compound	Velocity constant lit · min ⁻¹ · mole ⁻²	Ratio between velocity const.	Distribution constant, c
Water	$1.26 \cdot 10^{-4}$	4.80	13
Glycol	$6.05 \cdot 10^{-4}$		
Diglycol	$1.27 \cdot 10^{-3}$		
Ethanol	$1.29 \cdot 10^{-3}$	0.47	2.2
Ethylglycol	$6.10 \cdot 10^{-4}$		
Ethyldiglycol	$6.10 \cdot 10^{-4}$		
Diglycol	$1.27 \cdot 10^{-3}$		
		1.00	1
		2.08	2 ^{a)}

^{a)} Expected value.

DISCUSSION

Comparison between theoretical and experimental results shows that the theory presented accounts fairly well for the course of the reactions between ethylene oxide and reactive molecules. Especially significant is the result, that the distribution of products in the reaction with glycol or its ethyl ether closely follows a Poisson series, *i.e.* $c = 1$, see Table 1, Experiment Nos. 6 and 9. This is a direct proof of the assumption that all hydroxyl groups bound to an oxyethylene group have the same reactivity.

The value of the distribution constant c and, with it, the amounts of the higher glycol products increase with increasing alkalinity, Table 1, Experiment Nos. 1 to 5. This was also found to be the case by Davis, von Waaden, and Kurata¹². The large difference between the results with sodium carbonate (Experiment No. 4) and sodium hydroxide (Experiment No. 5) may seem noticeable. However, from published data¹⁸ for the velocity constants of the reaction between ethylene oxide and water, it may be calculated that, with the amount of sodium carbonate catalyst used, the catalysed and uncatalysed reactions are of comparable importance. Thus the value of c is intermediate between the values for uncatalysed and hydroxyl ion catalysed reactions.

A comparison between the quotients in Table 3 of the kinetical rate constants and the distribution constants c brings out some points of interest. The values agree in the case of the pair, ethylglycol — ethyldiglycol. For the pair ethyldiglycol — diglycol, the value predicted for c is 2 because the latter compound has two hydroxyl groups of the same reactivity as that of the single one of the former. This is in agreement with the experimental value from the velocity constants, 2.08. In the other cases there are discrepancies. Apart from experimental errors, these may have two causes. Firstly, the influence on the c -values of the differences in acidity of the various compounds are not accounted for by the kinetic experiments. Secondly, the rate constants were measured in different media which also differ from the media in the distribution experiments. Moreover, the medium changes during the reaction in the latter experiments, but it seems reasonable to assume that the distribution constants remain unchanged. The discrepancies ought to diminish as one passes to higher members in a reaction series, as is found to be the case for ethylglycol — ethyldiglycol. It should perhaps be observed that the rate constants given were determined at a much lower temperature than that used in the distribution experiments. For the early steps of the reaction series this difference may also have some influence on the velocity constant ratio.

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