Under similar conditions 2.5 g. of *p*-thiocresol and 4.3 g. of *n*-butylsulfonylmethyl bromide gave ditolyldisulfide and a product which did not crystallize. Recrystallization of the disulfide from alcohol gave 2.25 g. (90%), m. p. 45–46°.

Reaction with Phenylmagnesium Bromide.—To a solution of 0.15 mole of phenylmagnesium bromide in 70 ml. of ether was added with vigorous stirring a solution of 34.8 g. of IV in 400 ml. of ether. The addition required about one-half hour and the reaction mixture was refluxed an additional three hours, stirred for two hours without heating, and allowed to stand overnight. The residue remaining after filtration was washed with ether, suspended in iced hydrochloric acid and recrystallized from alcohol. The yield was 14.3 g. (56%) of methyl *p*-tolyl sulfone, m. p. 84–86°. The ether was removed from the filtrate of the reaction mixture by distillation from a water-bath through a fractionating column. The distillation residue was mixed with a little ether and ligroin (b. p. 70–90°) was added. The organometallic compound remaining was treated as before and gave 1 g. (3%) of IV. The ether-ligroin solution upon fractionation gave 18.2 g. (77%) of bromobenzene, b. p. 154–157°.

Reaction with Pyridine.—A solution of 12.5 g. of IV and 4.7 g. of pyridine in 100 ml. of absolute alcohol was refluxed for forty hours and the alcohol removed by distillation. The residue was diluted with 200 ml. of ether and the solid recrystallized from alcohol. This gave 1 g. (8%) of 1,2-di-*p*-tolylsulfonylethane, m. p. 201–202° which was identified by a mixed melting point with an authentic sample.[16] The ethereal solution was evaporated and the solid residue recrystallized from alcohol. This gave 9 g. (72%) of unreacted IV, m. p. 89–90°.

A similar experiment in which 2.15 g. of III was refluxed with pyridine in 25 ml. of alcohol for twenty-two hours gave 0.05 g. (2%) of 1,2-di-*n*-butylsulfonylethane, m. p. 177–179°, and 2.05 g. (95%) of unchanged III, m. p. 47–48°.

With Sodium Ethoxide.—To a sodium ethoxide solution prepared by dissolving 0.92 g. of sodium in 100 ml. of absolute alcohol was added 10 g. of IV and the mixture refluxed for fifteen hours. The solution was cooled, filtered and the solid washed with a little cold alcohol and then with water. There remained 0.2 g. of yellow, highly insoluble material which was not investigated further.[22] The alcoholic solution gave 5 g. (74%) of methyl *p*-tolyl sulfone, m. p. 85–86°, which was identified by a mixed melting point.

Other Results.—The recovery of unchanged bromosulfone was 80–95% in the following tests: (a) heating IV with two equivalents of tetrahydroquinoline at 100° for sixteen hours, (b) treatment of IV with two equivalents of dimethylamine for five days at room temperature and five hours at 40–50°, (c) refluxing IV for forty hours in 75% alcohol with two equivalents of potassium cyanide, (d) refluxing III for seven hours with two equivalents of sodium acetate in alcohol solution. No iodine was liberated when III and IV were treated with acidified potassium iodide under the conditions previously described.[7] No reaction occurred between III or IV and hydrazine hydrate under the conditions previously used[6] but VI reacted slowly, giving 3 ml. (8%) of nitrogen in five hours from 0.5 g. of the dibromosulfone.

Summary

Syntheses of three α-bromosulfones and one α,α-dibromosulfone have been described. The reactions of the α-bromosulfones showed that the sulfone group activates the halogen for oxidation reactions but deactivates it in metathesis reactions. The results suggest that the increased reactivity generally attributed to α-bromo-ketones, esters, etc., is due to preliminary reaction of the reagent with the unsaturated group, rather than to the polar influence of the group.

(22) This material was probably aldehyde resin. Willstätter and Hattenrote [*Ber.*, **43**, 1984 (1910)] reported the formation of aldehyde resins from the oxidation of alcohol by N-chloro compounds in which the hypochlorite character of the halogen is well known.

PHILADELPHIA, PENNA. RECEIVED MAY 24, 1940

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXI. The Mechanism of Polymerization of Ethylene Oxide[1]

BY STANLEY PERRY AND HAROLD HIBBERT

In contrast with the now almost universally accepted long chain structure of polymer molecules, there is not as yet an undisputed mechanism for the formation of such molecules in simple polymerization reactions. Two main theories are generally recognized: the Free Radical Theory, the chief proponent of which is H. Staudinger[2] and the Stepwise Addition Theory, due to Whitby.[3]

Staudinger assumes that the monomeric molecule is capable of yielding an intermediate having two free valence bonds; such free radicals are enormously reactive and hence add to one another with extreme ease, giving very long chains. This free radical chain reaction is supposed[4] to

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[1] From a thesis presented by Stanley Perry to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy (October, 1938). Part LX of this series, Perry and Hibbert, THIS JOURNAL, **62**, 2561 (1940).

[2] Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

[3] Whitby and Katz, THIS JOURNAL, **50**, 1160 (1928).

[4] Schulz and Husemann, *Z. angew. Chem.*, **50**, 767 (1937).

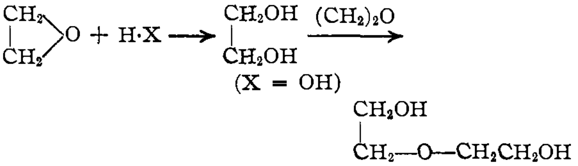
take place in three stages: (i) activation, in which the monomer takes up energy and becomes a free radical having two free valences; this is also assumed to be the slow rate-determining step; (ii) propagation, the rapid addition of the free radicals to one another in a series of chain reactions; it is assumed that the longer radicals are incapable of mutual addition; (iii) termination, in which the free valences become saturated, ending the reaction chains; this is assumed to occur by the addition of some compound H-X (where X is OH, OCH_2OH, NHR or similar group) and is believed to be slower than the propagation step.

Whitby proposed the stepwise addition theory to explain the polymerization of olefinic and diene substances, particularly styrene. The fundamental principle involved is merely that the monomer takes up energy of activation in the presence of a catalyst and adds another molecule of monomer with the migration of a hydrogen atom. The resulting polymer molecule remains activated and is able to add still more monomer molecules. The over-all rate is governed by the monomolecular activation process, while the final length of the chain produced depends largely on the rate at which the reactivity decreases with molecular complexity. The molecular chain retains throughout the process a group capable of further reaction under suitable conditions; in this respect the theory is in sharp contrast to the radical chain theory, which assumes a termination reaction rendering the growing chain molecules incapable of further growth.

As yet, the only definitely proven examples of long chain formation by a stepwise process involve condensation reactions which the proponents of the free-radical theory do not recognize as true polymerization processes. The question therefore arises as to what methods of approach are likely to afford conclusive proof of either theory. The only really valid proof of a step-wise process would seem to lie in the isolation of reactive intermediates for each type of polymerization; this is the method which has been adopted by Ziegler and co-workers[5] in work with diene polymers, and is also the method used in the present investigation of the specific case of ethylene oxide.

Mechanism of Polymerization of Ethylene Oxide.—Staudinger proposes two polymerization mechanisms for ethylene oxide, in which on the one hand relatively short chains only are formed and, on the other, both short and long chains. He suggests that the formation of all short chains takes place by the stepwise process first suggested for this reaction by Wurtz,[6] and ascribes to it a slow reaction velocity. The outside limit of chain growth by this method is set at ten or twelve repeating units. A second mechanism, namely, one involving free radicals, is therefore necessary to explain the formation of high polymers of ethylene oxide. Staudinger believes that as a consequence of the free-radical mechanism the reaction mixture contains at all times only the monomer and the completely polymerized inert product.[2]

In 1933, Hibbert and Perry[7] proposed the stepwise mechanism to account for the formation of both high and low polymers of ethylene oxide. This mechanism is as follows:



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + H{\cdot}X \longrightarrow \underset{(X\,=\,OH)}{\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}} \xrightarrow{(CH_2)_2O} \begin{array}{l}CH_2OH\\ |\\ CH_2{-}O{-}CH_2CH_2OH\end{array}$$

The reactions involved are those known to take place when ethylene oxide reacts with substances containing active hydrogen; the intermediates postulated in this connection always contain hydroxyl groups, no matter what the nature of the group X. The "reactive intermediates" of the mechanism (where water is the hydrogen-containing substance) are polyoxyethylene glycols $H(OCH_2CH_2)_nOH$. As part of the present investigation it is shown that the members of this polymeric series are identical in every way with the products formed in the polymerization of ethylene oxide (see Experimental Part). Since a number of these glycols have been synthesized by the authors[8] and shown to be pure products, it has been possible to test directly the reactivity of the postulated intermediates toward ethylene oxide, under the conditions of the polymerization reaction.

Polymerization by Aqueous Alkali.—Before considering the reactions of the postulated intermediates, a study was made of the effects of varying the ratios of water to ethylene oxide on the polymerization of the latter in the presence of a

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[5] Ziegler, Jakob, Wollthan and Wenz, *Ann.*, **511**, 64 (1934).

[6] Wurtz, *Compt. rend.*, **83**, 1141 (1876), and earlier papers.

[7] Hibbert and Perry, *Can. J. Research*, **8**, 102 (1933).

[8] Perry and Hibbert, *ibid.*, **14B**, 77 (1936).

constant concentration of caustic potash as catalyst. This is the method which is normally used to produce ethylene oxide polymers. In a series of eleven experiments, this ratio was varied from 10 to 0.01 (in terms of moles). The reaction products showed a gradual change in properties as the ratio was changed, the products formed by using the greatest proportion of water being thinly-viscous oils, changing through semi-solids to waxes to powders as the proportion of water decreased. The melting points of these products (Table I) show similar graduated changes, indicating that the extent of polymerization is increasing. This is further borne out by the observation (Fig. 1) that the percentage of non-distillable polymers increases as the proportion of water is decreased, and by the fact that the melting points of fractions (alcohol–ether) of each of the solid products were found to show a continuous range of values, up to 65° in some instances. The distillable polymers were fractionated repeatedly under reduced pressure; examination of the average boiling points of these fractions (Fig. 1) reveals that the polymerization reaction produces a continuous series of increasing chain-lengths. The final conclusion may therefore be drawn that polymerization of ethylene oxide by aqueous potash gives rise to a polymer-homologous series in which the variation in degree of polymerization between the least and most highly polymerized products may be very great, amounting, on occasion, to as much as 100 or more oxyethylene units.[9] It does not seem very likely that (as Staudinger's mechanism would require) the first ten members of this series of products are produced by an entirely different process, especially in view of the effect of the proportion of water on the final maximum chain length.

If, on the other hand, the stepwise mechanism is correct, a similar series of low and high polymers should be obtained by allowing ethylene oxide to polymerize in the presence of ethylene glycol alone (with caustic potash present in a constant small amount as the catalyst). This prediction was confirmed by the following experiments.

Ethylene oxide (11 g.) and potassium hydroxide (5 g.) were allowed to react at 20–25° with 155 g. of dry ethylene glycol, for a period of fourteen days. After removal of all unused reactant, a thinly viscous product (weight 22.8 g., corresponding to 86% reaction) was obtained, which could be distilled under reduced pressure into a series of fractions of graded distilling temperatures. The bulk of this material distilled below 128° at 3 mm. pressure, and no non-distillable residue was left. In two further experiments the same quantities and conditions were used, except that only 10% and 0.1%, respectively, of the above amount of glycol was employed. In the first case, the product was a highly viscous oil, still containing no non-distillable fraction but having a portion distilling only above 250° under a pressure of 0.02 mm. In the second case a semi-solid product was obtained, which contained over 90% of non-distillable members.

Furthermore, when the proportion of ethylene glycol used was small, all of it was observed to react with the ethylene oxide, none being recoverable from the reaction products.

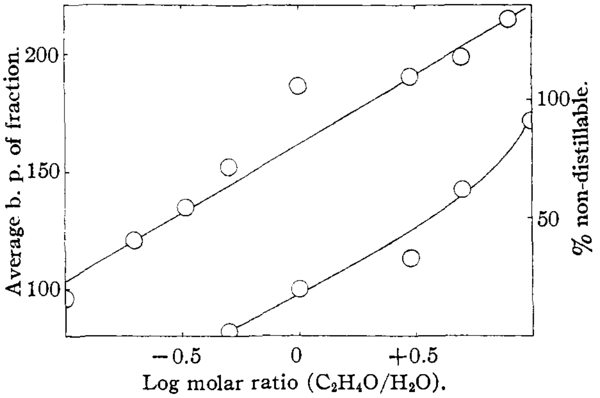

Fig. 1.—Effect of varying proportion of water on the properties of polymers from ethylene oxide.

Polyglycols as Intermediates.—That polyoxyethylene glycols are capable of acting on ethylene oxide to give long-chain polymers is fully established by the following experimental data. In these experiments, all moisture and air were rigorously excluded, and in some instances alkali metal was substituted for the hydroxide to avoid the formation of water in the actual reaction mixture.

Four experiments were carried out with diethylene glycol and ethylene oxide, the ratio of the weights of these reactants being widely varied. With the smallest proportion of glycol (mole ratio 1/100), the product was a hard, waxy solid, whereas the largest proportion (mole ratio 1/1) produced a viscous liquid; the intermediate proportions used (mole ratios 1/10, 3/100) gave products of graded consistency intermediate between these two extremes. A somewhat similar graduated series was obtained from trioxyethylene glycol (two expts.), tetraoxyethylene glycol (three expts.), pentaoxyethylene glycol (two expts.) and hexaoxyethylene glycol (three expts.). In the one experiment with octadecaoxyethylene glycol, 9.7 g. was used with 4.4 g. of ethylene oxide (in the presence of 0.05 g. of sodium as a catalyst); after fourteen days at 20–25° the

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[9] In the specific case of Expt. 7, liquid and solid polymers ranging from the monomer to solid polymers comprising at least 25 repeating units[3] were obtained.

product formed was a semi-solid white mass, in contrast to the thin liquid starting materials.

Thus, six polyglycols (n = 2, 3, 4, 5, 6 and 18) were used in varying concentrations, and in each case it was found possible to produce a series of reaction products of varying degrees of polymerization, by varying the proportion of glycol to monomer. It was thereby established that polyglycols as high as *eighteen units* long are capable of reacting with ethylene oxide, the relative amount of this reactant recoverable unchanged from the mixture rapidly decreasing with decreasing ratio of polyglycol to monomer.

The fact that high-molecular polymers can be prepared from the interaction of ethylene oxide and these polyoxyethylene glycols is a strong argument against the validity of the free radical mechanism of this polymerization, while at the same time it is in complete agreement with expectation based on the theory of a stepwise mechanism.

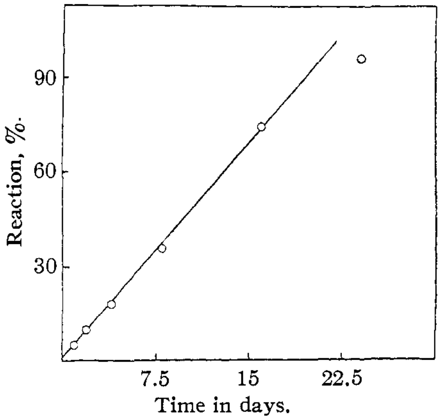

Fig. 2.—Polymerization of ethylene oxide in the presence of water and alkali.

Variation in Degree of Polymerization during the Polymerization Process.—According to the stepwise mechanism, the average degree of polymerization should increase linearly as the reaction proceeds. On the other hand, according to the free radical theory, the degree of polymerization should remain constant throughout the reaction. In order to test this point, six identical experiments (Table II) were begun simultaneously, each comprising water (1.8 g.), ethylene oxide (44 g.) and caustic potash (0.1 g.). The quantities used would normally lead to a final average degree of polymerization of about 17 units. The reaction was interrupted after periods of one, two, four, eight, sixteen and twenty-four days, respectively, a sample being analyzed after each time interval. It is evident from the data that the amount of polymer formed increases linearly with time (Fig. 2) and that the degree of polymerization gradually increases as the reaction proceeds, in agreement with the stepwise mechanism.

Polyethylene Oxides as Intermediates.—According to the stepwise mechanism, any of the products formed in an ethylene oxide polymerization, *even after the reaction is complete,* should be capable of further reaction with more ethylene oxide, to give still higher polymers. Again this is not to be expected on the basis of the free radical theory: consequently, this point has been subjected to direct experimental test. The initial reaction was carried out with ethylene oxide and pure dioxyethylene glycol (with a small amount of dissolved sodium to act as the catalyst), which according to Staudinger is incapable of adding to long-chain free-radical intermediates. The product, of average d. p. of about six units (Table II), was allowed to react with more ethylene oxide; the result of this was a new polymer having an average d. p. of 9 units. Further successive additions of ethylene oxide gave products of d. p. 12, 25 and 74 units, respectively.

Moreover, the amount of dioxyethylene glycol which could be recovered from the first product was only 45% of that originally present[10] and this had decreased to 29% in the second product: no unchanged dioxyethylene glycol could be obtained from succeeding products. Furthermore no distillable portions whatsoever could be obtained from the last two products. This demonstrates that the liquid products of the first two stages also reacted with the ethylene oxide. The assumption of a progressive series of reactive intermediates, postulated in the stepwise mechanism, would therefore seem to be amply confirmed by this series of reactions.

Supporting Evidence.—Certain other experimental facts are also in harmony with this point of view. Thus, absolute methyl and ethyl alcohols (in the presence of a small amount of catalyst) were found to react with ethylene oxide to give both liquid and solid polymers, depending as before on the proportions used. Aniline also gave a solid polymer. Ethylene glycol monomethyl ether gave a polymer with ethylene oxide,

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[10] Control experiments showed that with a mixture of only 7.6% of dioxyethylene glycol and non-distillable ethylene oxide polymers, 88% could readily be recovered, the remainder being merely held up in the distilling column.

the reaction being catalyzed with a small amount of solid sodium hydroxide, but under identical conditions the dimethyl ether did not react.

Attempts to find 1,4-dioxane among the products of the ethylene oxide polymerization were unsuccessful, although this substance is stable under the conditions of the reaction. In Staudinger's mechanism of ethylene oxide polymerization, there occurs a free-radical intermediate which corresponds empirically to this very stable ring-compound. It seems likely that some of the ring-compound would be formed if this reactive intermediate were actually present in the reaction mixture at any time.

Experimental

Ethylene Oxide.[11]—The anhydrous monomer was obtained by allowing ethylene oxide to stand over metallic calcium for a minimum period of two weeks. The dry reagent was then distilled directly into the reaction-bomb being used in the experiment.

Aqueous Ethylene Oxide Polymers.—In the first experiment, a mixture of ethylene oxide (44 g.), caustic potash (2.0 g.) and water (180 g.) was allowed to stand in a pressure bottle at 35° for fourteen days, after which it was cooled to −10° and opened. No ethylene oxide could be detected. The brown, viscous reaction mixture was neutralized with 5% hydrochloric acid and the water evaporated at 50° (15 mm.). The residual material was taken up in anhydrous ether (800 cc.) containing 5% of absolute ethanol to remove the inorganic constituents, and then decolorized with vegetable charcoal. The solvents were distilled off at 50° (15 mm.), using a minute stream of dry air to remove last traces; a constant weight of 60.8 g. was finally reached.

In expts. 2 to 12 of this series, the same procedure was followed, except that expts. 9 to 12 were given an additional two weeks at 60° in order to ensure complete reaction. When solid products were encountered, they were dissolved in distilled water before adding the acid.

The data are listed in Table I; one experiment was discarded because the yield was considerably below 90%.

Identity of Polyethylene Oxides with Polyoxyethylene Glycols.—Chemical proof of the identity of the two series was obtained as follows. The first member of the series obtained from ethylene oxide was converted into the cyclic acetal of *p*-nitrobenzylidene glycol by the method of Hibbert and Sturrock[12] in a yield of 27.1 g. from 10 g. of the fraction. The melting point of the derivative (90.0–90.5°) agreed with that given by Hibbert and Sturrock for the material obtained from ethylene glycol; this was confirmed by a mixed melting point, and by comparison of the physical properties of ethylene glycol with those of the polyethylene oxide fraction.

The fraction corresponding to hexaoxyethylene glycol was found to have the same distilling range and refractive index as the synthetic product.[8] Furthermore, treatment of this fraction (8.0 g.) with thionyl chloride (4.4 g.) in pyridine (2.9 g.) solution gave 6.5 g. of an oil which on fractionation yielded 5.2 g. of a compound of b. p. 146–149° (0.013 mm.) and refractive index 1.4655 (20°), identical with synthetic hexaoxyethylene dichloride.[8] *Anal.* Calcd. for $C_{12}H_{24}O_5Cl_2$: Cl, 22.23. Found (Stepanow volumetric method): Cl, 22.14, 22.10.

Reactivity of Polyethylene Oxides. Stage 1.—Freshly-distilled dioxyethylene glycol (18 g.) containing freshly-cut metallic sodium (1 g.) was allowed to react with anhydrous ethylene oxide (14 g.) in a sealed pressure bottle under an atmosphere of nitrogen for seven days at 20°. The mixture became very viscous. The bottle and contents were weighed, cooled to 0°, opened and immediately placed under reduced pressure (10 mm.) at 40°. There was no liberation of gas or loss of weight, showing that ethylene oxide was absent. Of a total product of 33 g., 12.2 g. was removed and purified in the manner described above. **Stage 2.**—The balance of the reaction product (20.8 g.) was mixed with ethylene oxide (17.6 g.) in a bomb under nitrogen and re-sealed; this mixture was allowed to stand for eight days at 20°. The reaction mixture was finally treated as in Stage 1. The procedure was repeated for five stages. The samples obtained from each stage were then

TABLE I

AQUEOUS ETHYLENE OXIDE POLYMERS

H_2O per mole C_2H_4O, g.	M. p. of product, °C.	H_2O per mole C_2H_4O, g.	M. p. of product, °C.	H_2O per mole C_2H_4O, g.	M. p. of product, °C.
54	−32 to −30	6	2 to 4	0.9	47 to 49
36	−21 to −19	3.5	13 to 15	.45	51 to 53
18	−17 to −15	1.8	31 to 33	.18	57 to 59

TABLE II

CHANGE IN DEGREE OF POLYMERIZATION WITH PROGRESS OF REACTION

Reaction time, days	Percentage reaction	M. p. of product, °C.	Refractive index of product (60°)
1	5	5–7	1.4450
2	9.8	28–30.0	1.4550
4	17.7	30–32.0	1.4556
8	35.4	30–33.5	1.4561
16	74.3	45–47.0	1.4563
24	96.1	47–49.5	1.4578

TABLE III

PRODUCTS FROM A STEPWISE SERIES OF REACTIONS

Sample	M. p. of product, °C.	Refractive index of product (60°)	Av. mol. wt.
Stage 1	−19 to −17	1.4507	287
Stage 2	9 to 11	1.4536	424
Stage 3	20 to 22	1.4545	536
Stage 4	40 to 43	1.4571	1090
Stage 5	54 to 58	1.4579	3270

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[11] Experimentation with ethylene oxide must be classed as dangerous. Polymerization reactions, being exothermic, occasionally and unexpectedly lead to very rapid development of high pressures, sufficient to shatter a stout container. A particularly violent explosion occurred in the course of this investigation as a result of an accidental leakage of ethylene oxide into the confined space of a fume chamber and ignition of the resulting ethylene oxide–air mixture from either an electric hot-plate or an open flame in an adjoining cupboard. The percentage of ethylene oxide required to form such mixtures is very low.

[12] Hibbert and Sturrock, THIS JOURNAL, **50**, 3374 (1928).

examined, with the results shown in Table III. The cryoscopic molecular weight determinations were carried out in 1,4-dioxane, purified according to the method of Eigenberger.[13] Two concentrations were used, and the average value obtained did not differ by more than 3% from the individual results.

Summary

The hypothetical intermediates of the stepwise polymerization of ethylene oxide, namely, the pure synthetic polyoxyethylene glycols, have been shown to react with ethylene oxide in the presence of a catalyst to give higher polymers. This reaction takes place even with the eighteen-membered glycol. It has also been shown that the polymerization products from ethylene oxide are capable of reacting further with the monomer. On the basis of this and other evidence, it is concluded that ethylene oxide polymerizes by a stepwise series of reactions.

MONTREAL, CANADA RECEIVED JUNE 8, 1940

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[13] Eigenberger, *J. prakt. Chem.*, [2] **130**, 75 (1931).

[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE COMMERCIAL SOLVENTS CORPORATION]

β-Dioximes and Trialkylisoxazoles from Nitroparaffins

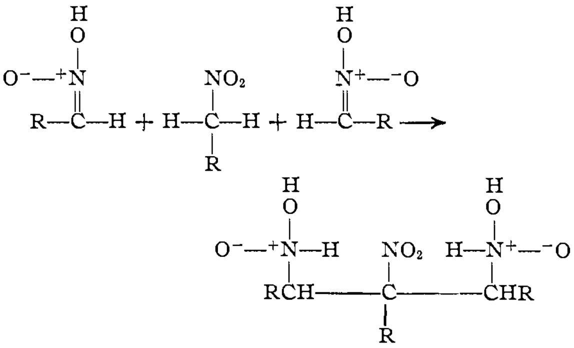
BY SAMUEL B. LIPPINCOTT

Early investigators[1,2] in the field of nitroparaffins discoverd a very interesting reaction in which trialkylisoxazoles are produced from primary nitroparaffins of more than one carbon atom in the presence of basic substances. By employing milder conditions than those used by the earlier investigators a new compound has been isolated from each of the nitroparaffins, nitroethane, 1-nitropropane and 1-nitrobutane. Upon refluxing with dilute acids each of these new compounds yields one mole of hydroxylamine and one mole of trialkylisoxazole. This fact, together with the analyses of the compounds, has led to the conclusion that they are β-dioximes of the general formula RC(=NOH)CHRC(=NOH)R. Dunstan and his co-workers suspected that derivatives of the β-dioximes were precursors of the trialkylisoxazoles but they were unable to isolate any such products. They therefore proposed a mechanism for the reaction that did not include any such intermediate. The following mechanism is now proposed.

Step 1.—In the presence of mild bases the nitroparaffin exists in the two forms, normal and *aci*.

$$\mathrm{RCH_2NO_2 \rightleftarrows RCH{=}NOOH}$$

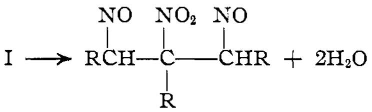
Step 2.—A condensation takes place in which two molecules of the *aci*-form unite with one molecule of the normal form.



$$\mathrm{R{-}CH{=}\overset{+}{N}(OH){-}O^{-} + H{-}C(R)(NO_2){-}H + H{-}C(R){=}\overset{+}{N}(OH){-}O^{-} \longrightarrow RCH[\overset{+}{N}H(OH){-}O^{-}]{-}C(R)(NO_2){-}CHR[\overset{+}{N}H(OH){-}O^{-}]}$$

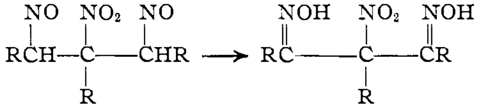
I

Step 3.—This molecule loses two molecules of water.



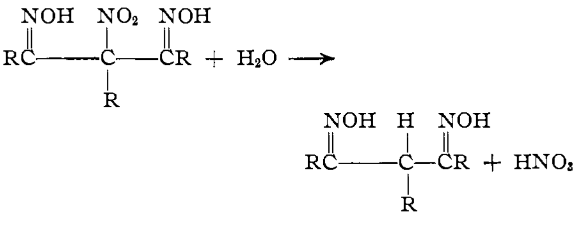
$$\mathrm{I \longrightarrow RCH(NO){-}C(R)(NO_2){-}CHR(NO) + 2H_2O}$$

Step 4.—The nitroso groups rearrange to isonitroso or oxime groups.



$$\mathrm{RCH(NO){-}C(R)(NO_2){-}CHR(NO) \longrightarrow RC({=}NOH){-}C(R)(NO_2){-}C({=}NOH)R}$$

Step 5.—Under the influence of the negative oxime groups the nitro group is lost by hydrolysis.



$$\mathrm{RC({=}NOH){-}C(R)(NO_2){-}C({=}NOH)R + H_2O \longrightarrow RC({=}NOH){-}CH(R){-}C({=}NOH)R + HNO_3}$$

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[1] Dunstan and Dymond, *J. Chem. Soc.*, **59**, 410 (1891).

[2] Dunstan and Goulding, *ibid.*, **77**, 1262 (1900).