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A Novel Way for Ethoxylation with Basic Catalysts

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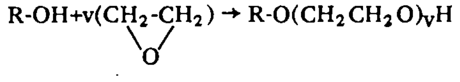
ABSTRACT

Ethoxylation of dodecyl alcohol catalyzed by alkali hydroxides are accelerated by adding complexing agents for the alkali ions. The rate of ethoxylation could be increased by crown ether and dodecyl alcohols of a higher degree of ethoxylation. The effect is more pronounced with the crown ether; thus, reactions not taking place under other circumstances could also be carried out. The complexing additives have no significant effect on the molar mass distribution. The reaction could also be accelerated by using more bulky organic cations (e.g., triethylbenzylammonium ion) instead of the alkali cation.

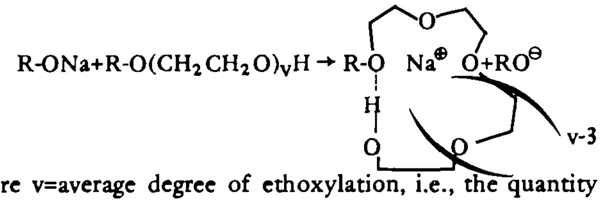
INTRODUCTION

In our earlier papers, the reaction of ethylene oxide and fatty alcohols has been studied in detail. A reproducible method for ethoxylation has been elaborated (1,2), together with methods for product analysis (3-7).

In the course of ethoxylations catalyzed by alkali hydroxides, the Weibull-Törnquist effect has been confirmed (8,9), i.e., it has been established that the distribuion coefficients calculated according to Natta and Mantica (10) change with the average degree of ethoxylation: with the progress of the reaction they decrease and approach a limiting value. This phenomenon was interpreted in terms of complexing of the homologues of a higher degree of ethoxylation with the alkali ions, thereby facilitating the formation of isolated alkoxide ions. Their reactivity is higher than that of anions in a contact ion pair.



$$R\text{-}OH + v(CH_2\text{-}CH_2) \rightarrow R\text{-}O(CH_2CH_2O)_vH$$



where v=average degree of ethoxylation, i.e., the quantity (mol) of ethylene oxide reacted with one mol of starting compound.

On the basis of this phenomenon we have tried to accelerate the reaction by complexing compounds previously introduced into the reaction mixture, which can bring about the above effect at the start of the process. Dodecyl alcohol of a higher degree of ethoxylation and crown ethers have been used for this purpose.

EXPERIMENTAL

Ethoxylations were carried out in a semimicro apparatus based on the measurement of the volumetric flow (Fig. 1). The reactor has to be oxygen-free, because of safety requirements connected with work with ethylene oxide (11, 12) and quality requirements concerning the products. This was ensured by a preliminary flushing of the system with nitrogen. Nitrogen streams from bomb 8; ethylene oxide flows from bomb 2 into three-way valve 3. From there, the gas flows through buffer vessels 4 and 5 and capillary flowmeter 6 (differential manometer) into the reactor 7 where it bubbles through the substrate reacting with it, while the remainder leaves the system through buffer vessel 8 and capillary flowmeter 9.

Isothermal conditions for reaction were ensured by a boiling liquid bath **10** heated by an electric heater **12**. Reaction heat was consumed by the latent heat of the boiling liquid. The end-point of the reaction was estimated from the difference between the volume rates of ethylene oxide at the inlet and outlet of the reactor.

The accurate amount of ethylene oxide taken up and the average degree of ethoxylation (v) was determined from the increased of the mass of the reaction mixture.

Dodecyl alcohol ("Alfol-12", produced by Condea) (0.02 mol) was used in each experiment. NaOH, KOH (Reanal) and triethylbenzylammonium hydroxide (Merck) were used as catalysts.

The ethoxylation of alcohols does not lead to uniform products, a mixture of polymer homologues is formed as a result of a competitive-consecutive reaction.

Product composition i.e., the distribution of these polymer homologues, was determined by gas chromatography, as described earlier (9).

RESULTS AND DISCUSSION

Ethoxylation in the Presence of Dodecyl Alcohols of Higher Degree of Ethoxylation

In the experiments, dodecyl alcohol of an average degree of ethoxylation of ca. 10 was used. It was prepared by ethoxylation catalyzed by alkali hydroxide. Rates of the reactions with and without this additive are summarized in Table I. From these data it can be seen that the rate of ethoxylation can be increased by more than 20% by the addition of this compound of a higher degree of ethoxylation. The effect decreases with increasing temperature. The molar mass distribution of the products obtained agrees with that of the reaction without additive within the error limit (Table II).

TABLE I

Rate of Ethoxylation of Dodecyl Alcohol in the Presence of C_{12}-10 Ethylene Oxide

Catalyst Name	Catalyst %	Additive %	Additive v	Temperature (C)	Rate ratio with/without additive
NaOH	3	4	9.59	140	1.20
	3	4	9.59	100	1.76
	3	4	9.59	180	1.22
KOH	3	4	9.83	140	1.21
	33	4	9.83	100	1.60
	5	5	9.83	100	1.32

C_{12}-10 EO: dodecyl alcohol with an average degree of ethoxylation of 10.

TABLE II

Molar Mass Distributions of Products with and without Additive

Catalyst	Additive	X_0	X_1	X_2	X_3	X_4	v
NaOH	–	0.196	0.138	0.162	0.157	0.094	2.50
NaOH	+	0.200	0.141	0.167	0.153	0.100	2.50
KOH	–	0.209	0.142	0.168	0.390	0.102	2.50
KOH	+	0.210	0.147	0.165	0.130	0.092	2.50

X_0: Fraction of dodecyl alcohol. X_i: Mol fraction of dodecyl alcohol containing i mol ethylene oxide.

Thus, in cases when products of a higher degree of ethoxylation are desired, it is conventient to add 3-5% of the previous production to every new reaction, as it accelerates the first period of the reaction, thereby increasing the capacity of the apparatus.

Ethoxylation in the Presence of Crown Ethers

A more significant effect can be expected from crown ethers. We used 18-crown-6 (Fluka) in our experiments. Results of ethoxylation are summarized in Table III.

It is apparent from the data of Table III that the rate-increasing effect of the crown ethers is superior to that of dodecyl alcohols of higher degree of ethoxylation. This effect is especially significant at lower temperatures. The

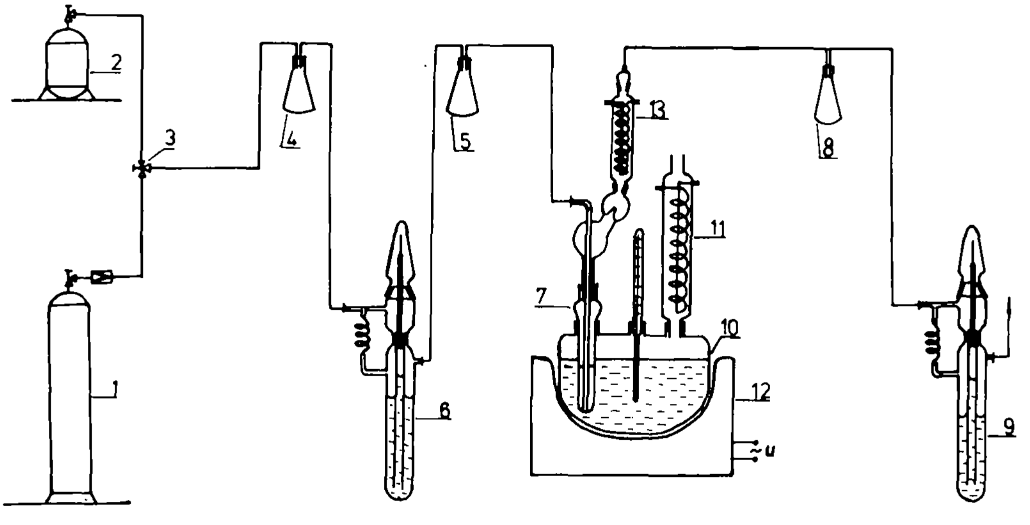


FIG. 1. Apparatus for ethoxylation.

TABLE III

Ethoxylation of Dodecyl Alcohol in the Presence of Crown Ether

Catalyst Name	Catalyst %	Crown ether %	Temperature (C)	Rate ratio with/without crown ether
KOH	3	3	140	2.37
	3	6	140	2.57
	3	0.8	140	0.98
	3	3[a]	140	1.47
	5	5	180	8.57
NaOH	3	3	100	2.83
	3	3	140	2.17
	3	3	180	1.22
	5	5	80	3.07

[a] Measured with dicyclohexyl-18-crown-6.

crown ether also makes the ethoxylation possible in cases when there is no reaction at all without it (at 80 C, in the presence of 3% of the catalyst).

The crown ether should be added expediently in a molar ratio of 1:1 with respect to the alkali hydroxide. (There is hardly any change for a molar ratio of 2:1 in the reaction rate as compared to the 1:1 ratio; the addition in a molar ratio of 1:4 has no effect at all.) The effect is more pronounced with KOH, probably due to the more advantageous atomic diameter (13).

Crown ethers have no significant effect on the molar mass distribution. Ethoxylating 1-butanol, Ovrik (13) found product distributions shifted to lower molecular weight adducts when the molar ratio of crown ethers to the alkali metal hydroxides was higher than 1:1. Even his experiments showed no significant changes in the product distribution if the molar ratio was kept between 0:1 and 1:1. The distributions obtained approach the theoretical Weibull-Nycander-Gold distribution (14) more closely than those obtained without additives (Table IV). In the presence of crown ethers, the kinetics of ethoxylation is somewhat modified compared to that without crown ethers; the ethylene oxide uptake is not linear with time, it decelerates a little, but it still exceeds that of the reaction containing only alkali hydroxide (Fig. 2).

TABLE IV

Distribution in the Presence of Crown Ether

Catalyst	Additive	X_0	X_1	X_2	X_3	X_4	v
NaOH	–	0.215	0.143	0.168	0.160	0.095	2.5
NaOH	+	0.220	0.143	0.173	0.166	0.129	2.5
Theoretical distribution		0.220	0.142	0.172	0.166	0.130	2.5

Ethoxylation in the Presence of Quaternary Ammonium Hydroxide

It is known that in nucleophilic substitution reactions the reactivity of the nucleophilic anion in the ion pair is increased if the diameter of the counter ion, the cation, increases (15).

This effect probably also plays a role in the increase of the reactivity of the cation enclosed in the complex during ethoxylation. We tried to achieve this effect also by forming the alkoxide with a greater cation than the alkali metal cations. Triethylbenzylammonium hydroxide catalyzed the reaction well at 80 C, but it was ineffective at higher temperatures. The catalytic effect ceased to exist after a certain reaction time (200 min), but until this time, the triethylbenzylammonium hydroxide efficient than either alkali hydroxide used. The distribution of the products obtained is that of the Weibull-Nycander-Gold type (Fig. 3).

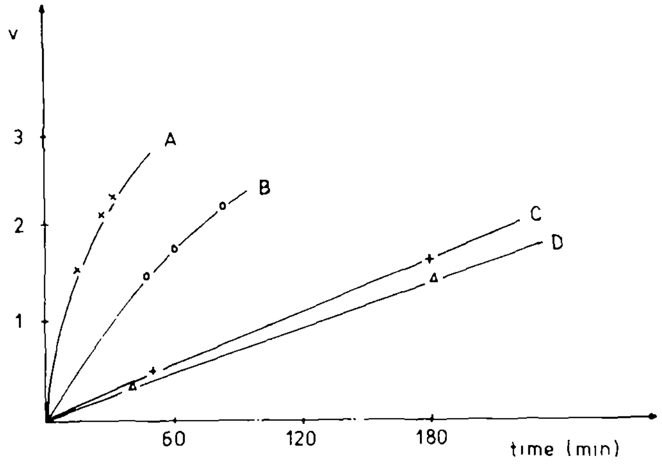


FIG. 2. Effect of crown ether on ethoxylation. (A) KOH + crown ether; (B) NaOH + crown ether; (C) KOH; (D) NaOH.

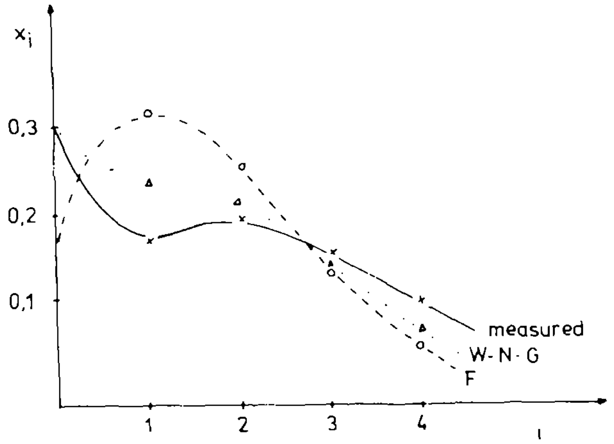


FIG. 3. Molar mass distribution of ethoxylation products obtained with triethylbenzylammonium hydroxide as catalyst. W-N-G: distribution according to Weibull, Nycander and Gold. F: distribution according to Flory.

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