Ethoxylation of Fatty Amines

H. L. SANDERS, J. B. BRAUNWARTH, R. B. McCONNELL and R. A. SWENSON,
Varney Chemical Div., Northern Petrochemical Co., Janesville, Wisconsin 53545

Abstract

It is well known that long chain alcohols and phenols cannot react with ethylene oxide in the absence of catalysts, whereas primary fatty amines can take up at least two moles of oxide to form tertiary amines. It has been found that further ethoxylation of this two mole adduct in the absence of added catalyst can proceed only if ethoxylation temperatures are lowered considerably. The present paper demonstrates that this low-temperature ethoxylation is really catalyzed by a previously overlooked highly alkaline compound generated during the course of the reaction. It is shown that this is a long-chain quaternary ammonium compound, and the mechanism of its formation is described. As the addition of ethylene oxide proceeds, this quaternary gradually decomposes and the reaction essentially comes to a halt when it has all disappeared.

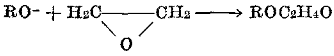
Introduction

Interest in the reaction mechanisms of ethylene oxide additions has increased over the years as the volume of nonionic surfactants produced has risen to about 400 million pounds annually and promises to expand even further.

A voluminous literature exists on the ethoxylation of linear alcohols, alkyl phenols and fatty acids (1). In general it has been found that these reactions do not proceed at all in the absence of catalysts. Alkalies are very effective initiators however, and reaction rates increase with basicity of the catalyst employed.

The mechanism of these reactions is believed to involve formation of a carbanion whose negative charge induces nucleophilic cleavage of the ethylene oxide ring:

$$\mathrm{ROH + NaOH \longrightarrow RONa + H_2O}$$



$$\mathrm{RO^- + H_2C\!-\!CH_2\ (\text{via }O) \longrightarrow ROC_2H_4O^-}$$

Much less attention seems to have been paid to the reaction of ethylene oxide with fatty amines, even though this class of nonionic surfactants has achieved industrial importance in the emulsifier field. An excellent brief review of this field is given by Shapiro (2).

Perhaps the best work on the subject has been carried out by Komori and co-workers (3,4), who demonstrated that fatty amines could react with ethylene oxide, under certain conditions, without any added catalyst being required. In view of the rather unusual results obtained, it was decided to repeat some of this work.

Experimental Procedures and Discussion

In all of these studies a stirred, stainless steel Parr autoclave was used. High quality commercial ethylene oxide (0.001% water, by weight) was forced by nitrogen into the autoclave from an oxide reservoir mounted on a scale so the amounts added could be followed by weight loss. Figure 1 is a photograph of the equipment used.

The first series of experiments involved addition of ethylene oxide to distilled primary lauryl amine (Formonyte D616, Foremost Chemical Co., Oakland, Calif.) at various temperatures, with and without NaOH catalyst. Low pressures of 5–10 psig were used in order to simulate Komori's conditions.

The procedure used was to bring the amine in the reactor to about 110 C, and vacuum strip at 20 mm for an hour to remove traces of water and carbonate. Then ethylene oxide was added in increments, while periodically withdrawing samples (through the sampling tube) for analysis. By running neutralization equivalents on the samples (titration with 0.25N HCl to Bromphenol Blue) the molecular weight obtained showed the amount of oxide added at any point and served as a check on the weight losses read off the scale. Figure 2 shows the results of three uncatalyzed runs and one run in which 0.05% NaOH was added to the starting amine.

In the uncatalyzed series it can be seen that at high temperature (230 C) only 2 moles of oxide could be added, after which the reaction stopped completely and no more could be added. In runs at 120 C and 90 C, however, about 4 moles and 10 moles of ethylene oxide could be added, respectively, before the reaction essentially came to a halt. Rather surprisingly, it seems that lower temperatures favor oxide uptake, contrary to most conventional ethoxylations.

It should be noted, however, that overall rate of reaction is not increased at lower temperatures—only the total amount reacted. At low temperatures very long induction periods are encountered, but when reaction starts the velocity is very high.

On the other hand, addition of 0.05% NaOH to a high temperature run (230 C) greatly increased

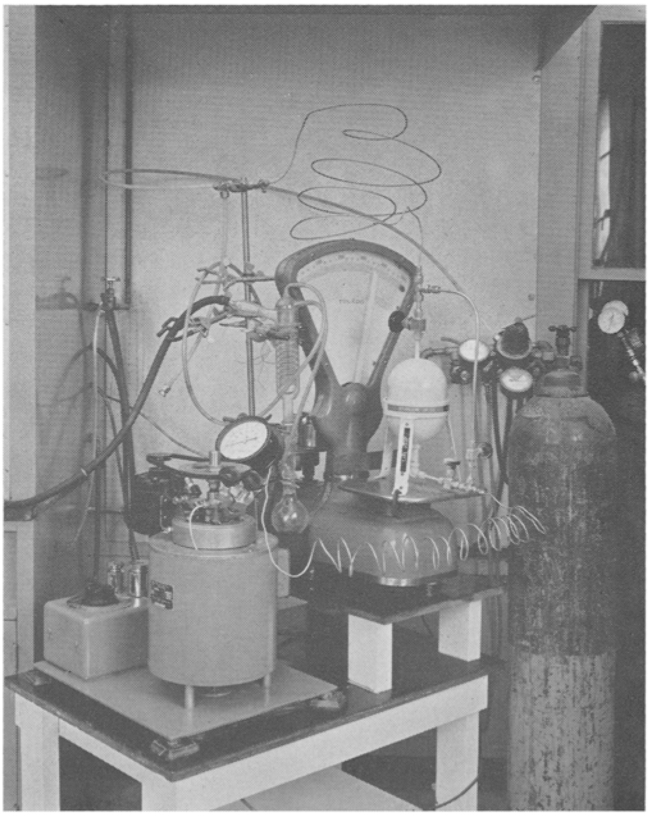


FIG. 1. Ethoxylation equipment.

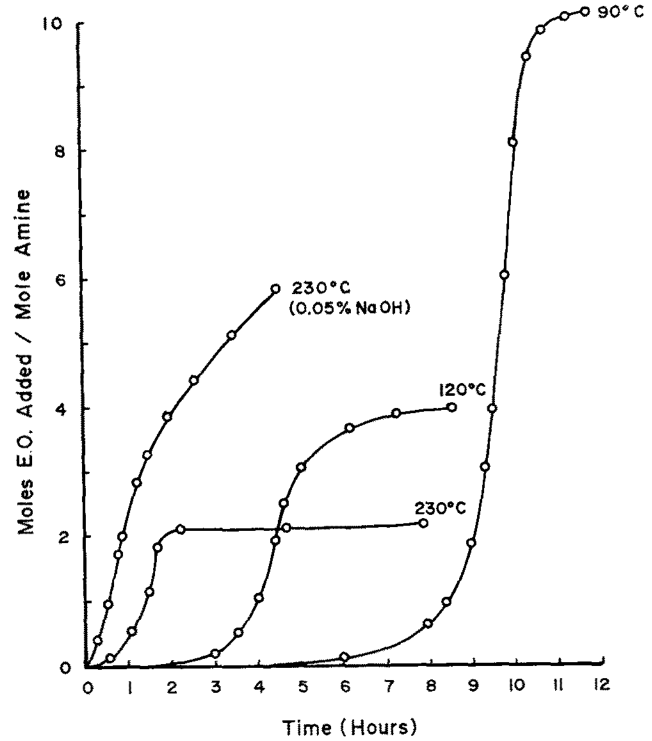


FIG. 2. Degree of ethoxylation at various temperatures.

both the amount reacted and the reaction velocity. Thus the long induction periods disappeared and considerable amounts of oxide could be added, showing the catalytic effect of strong alkali even at low concentrations.

Up to this point the results obtained confirm those of Komori. However, a new and puzzling phenomenon was noted when pH measurements of the ethoxylates were made. For example, when the 2-mole adduct from the caustic-catalyzed run was made into a 5% solution in 50% aqueous alcohol, a pH of 11.4 was found with the glass electrode. On the other hand, the 2-mole adduct from an uncatalyzed run (120 C) showed a pH of 12.0. Thus a product without added alkali unexpectedly shows a higher pH than the same material with caustic present.

It was observed that products with pH values over 10.0 were red to phenolphthalein indicator in anhydrous isopropanol. Therefore the amount of acid required to discharge the red color was taken as a measure of the strong alkali or free base present.

To investigate the nature of this high alkalinity in uncatalyzed reaction products, titrations were carried out with 0.25 N HCl to the phenolphthalein endpoint in isopropanol solutions, thus measuring the actual amounts of strong base present. The procedure consisted of taking samples at various points during the ethoxylation runs and rapidly titrating as above to determine the basicity, expressing the results as milligrams of KOH per gram. Figure 3 shows the results obtained.

From the three uncatalyzed runs plotted, it is seen that almost no strong base (i.e., alkaline to phenolphthalein) forms at all during the high temperature run at 230 C. On the other hand, at 120 C the basicity rises to a maximum when about 2 moles of oxide are added to the lauryl amine, then drops off; at 90 C the maximum is reached at about 3 moles added.

Comparing Figures 2 and 3, it is also interesting to note that the basicity approaches zero at about the same degree of ethoxylation as where the reaction

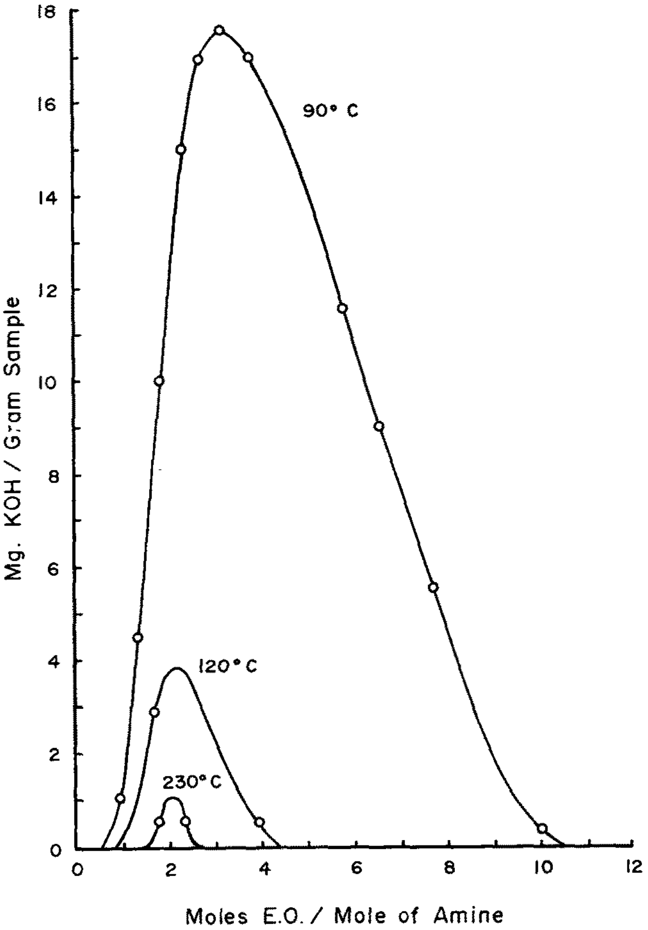


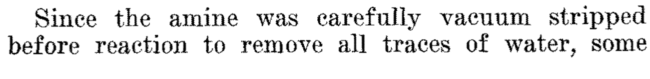
FIG. 3. Amount of free base formed at various temperatures.

essentially comes to a halt. Thus at 90 C basicity drops off to nearly zero after about 10 moles of oxide are added, which is about where the ethoxylation addition also tapers off; similar results are seen for the 120 C run at the 4 mole point.

From the foregoing it would be logical to conclude that a highly alkaline substance is being generated during the uncatalyzed ethoxylation of lauryl amine, and that ethoxylation ceases when this substance disappears by thermal decomposition.

In order to test this theory in a different way, a pure sample of lauryl N,N-bis (hydroxyethyl) amine was synthesized from lauryl chloride and diethanolamine, thus producing the 2-mole adduct by a different route. It was found that this product had a pH of 10.0 in aqueous alcohol but contained no free base, i.e., was not red to phenolphthalein in anhydrous isopropanol. However, when this compound was then reacted with ethylene oxide at 120 C, without added catalyst, free base immediately appeared. It would seem, therefore, that the base is formed only during reaction with ethylene oxide, and at moderately low temperatures.

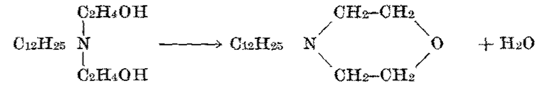
One hypothesis would be to assume that this basic substance is a quaternary ammonium hydroxide, since such compounds are known to be both highly alkaline and relatively temperature unstable. If water were present, quaternaries could readily form by the following well known reaction (5):



$$C_{12}H_{25}\text{-}\overset{\displaystyle C_2H_4OH}{\underset{\displaystyle C_2H_4OH}{N}} + H_2C\underset{O}{\text{——}}CH_2 + H_2O \longrightarrow \left[C_{12}H_{25}\overset{\displaystyle C_2H_4OH}{\underset{\displaystyle C_2H_4OH}{N}}\text{-}C_2H_4OH \right] OH$$

Since the amine was carefully vacuum stripped before reaction to remove all traces of water, some other source of water must be found for the above reaction to occur.

It was theorized that one possible mechanism could involve the formation of lauryl morpholine from the 2-mole adduct by splitting out of water and ring closure, as follows:



This reaction has even been patented as a commercial process (6). Therefore if the presence of lauryl morpholine in the uncatalyzed ethoxylation product could be demonstrated, the origin of the water would be evident. Of course, the water would not exist, as such, in the reaction, being converted to quaternary ammonium hydroxide instantaneously.

Unfortunately, attempts to isolate lauryl morpholine from the 2-mole adduct using various wet adsorption techniques were unsuccessful. A gas chromatographic analysis was therefore used, as follows:

A Perkin-Elmer 820 Chromatograph was used with a 6 ft × 0.125 in. 10% DEG Succinate, AW-DMS, Chrom G column, an injection temperature of 300 C, oven temperature of 200 C, detector temperature of 280 C, and a chart speed of 0.5 in. per minute. A 0.5 microliter sample of coco morpholine (Baird Chemical Co., New York), containing C_{12}, C_{14}, C_{16}, C_{18} alkyl morpholines was run through to obtain a reference curve (Fig. 4, upper half). Next, a portion of a 2-mole adduct (containing maximum free base) from a coco amine ethoxylated at 120 C was treated with trifluoroacetic anhydride. This makes a more volatile derivative of the ethoxylated amine by esterification of the hydroxyl groups, leaving any coco morpholine present unaltered. Then a 6 μliter sample was run through the column (Fig. 4, lower half).

As can be seen, the predominant coco morpholine peaks appear in both runs, thus confirming its presence in the 2-mole adduct. Measurements indicated that about 3% alkyl morpholine was present.

Assuming the above mechanism of free base generation to be correct, it was reasoned that a different kind of adduct, less apt to ring-close and form morpholine compounds, would not yield quaternary base during ethoxylation. To test this, pure lauryl N,N-bis (2-hydroxypropyl) amine was prepared from lauryl chloride and diisopropanolamine. This compound should not form a morpholine ring readily because of steric hindrance. On attempting to react this with ethylene oxide at 120 C without added catalyst, it was found that no free base formed and no addition of ethylene oxide occurred, which tends to confirm the above theory of quaternary ammonium hydroxide formation during ethoxylation of fatty amines.

A sample of the lauryl N,N,N-tris (hydroxyethyl) ammonium hydroxide quaternary believed to be present was synthesized by reacting lauryl N,N-bis (hydroxyethyl) amine with ethylene chlorhydrin and treating with silver oxide. The product was a colorless, viscous, aqueous solution exhibiting extremely high alkalinity. As expected, it was very unstable, turning dark brown immediately on slight warming.

It should be mentioned at this point, that the Komori and Karaki paper (4) specifically states that no quaternary is formed during the ethoxylation of lauryl amine. This statement appears to be based on their analytical results, in which the amine values, or molecular weights, found by titration agreed fairly well with the theoretical values based on the weight of oxide added, thus apparently leaving no room for quaternaries. In addition, by reacting some of the adducts with benzyl chloride at 120 C, they found that the expected amounts of lauryl di (hydroxyethyl) benzyl chloride quaternaries were obtained. All of this evidence seemed to confirm the absence of any extraneous material in the ethoxylates.

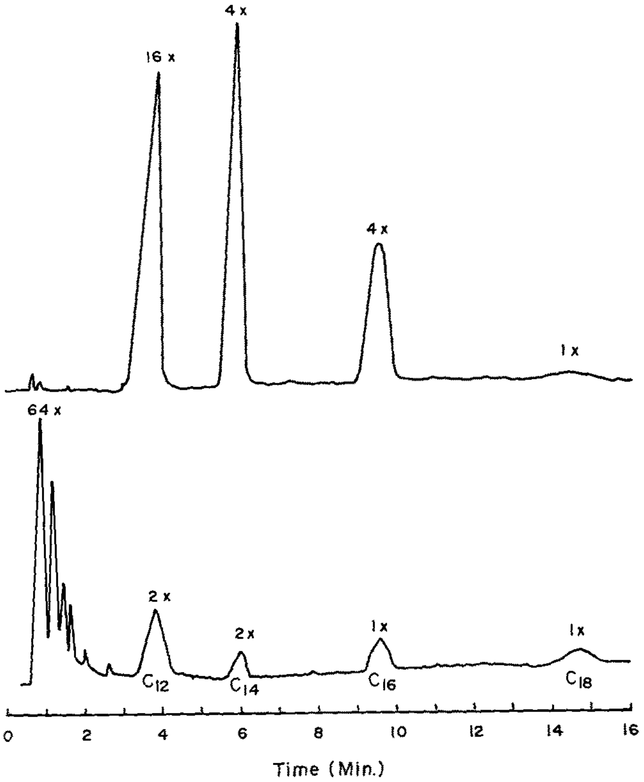


FIG. 4. Chromatograms of coco morpholine (top) and trifluoroacetyl-treated 2-mole adduct of coco amine (bottom).

This reasoning is based on the tacit assumption that any quaternary formed during the ethoxylation would be heat stable and not titratable as chloride quaternary. It has been found in the present investigation, however that both of these premises are incorrect. The tris (hydroxyethyl) quaternary generated during the ethoxylation is so unstable that it is largely destroyed during the analytical processing operations and reverts to tertiary amine, thus escaping detection. Furthermore this hydroxide quaternary would titrate with silver nitrate just like a chloride quaternary, again escaping detection.

In seeking an explanation for the fact that ethoxylation of lauryl amine proceeds farther at lower temperatures, the Komori study concludes that tertiary amines are the active catalysts. To prove this they ethoxylated lauryl alcohol in the presence of an equimolar amount of lauryl dimethyl amine. The reaction was found to proceed at lower temperatures much faster than at high temperatures, just as with the ethoxylation of amines. Since the ethylene oxide must have added to the alcohol, it would seem that the tertiary amine had a catalytic effect in some way (by hydrogen bonding, according to Komori).

This experiment was repeated for the present study (vacuum stripping at the start to eliminate water) and the reaction was found to proceed readily at 65 C. However, a considerable amount of free base was found to form. Since the dimethyl laurylamine cannot form morpholine rings and thus generate water, it is at first sight difficult to account for this free base.

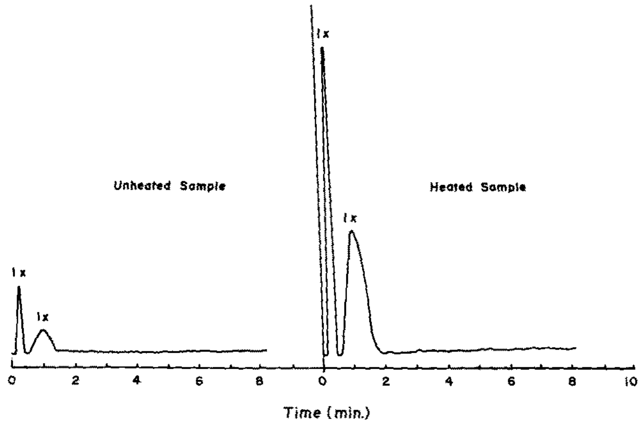
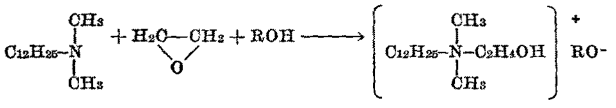


FIG. 5. Chromatograms showing decomposition products of quaternary ammonium butoxides on heating.

An alternative route, however, could be through formation of a quaternary ammonium alcoholate rather than the hydroxide, with the fatty alcohol replacing water as the proton donor, thus:



Such an alcoholate would be as alkaline as the hydroxide.

To test this theory a blend of 4 moles of *n*-butanol with 1 mole dimethylaurylamine was ethoxylated at 40 C without added catalyst. Addition began immediately with no induction period. Free base also began to form immediately, increasing to 28 mg KOH per gram soon after starting. This is about 10 times the amount generated during ethoxylation of laurylamine at 120 C, which would be anticipated in view of the combination of low temperature (little thermal decomposition of the quaternary) and high concentration of proton donor (alcohol). About 4 moles of ethylene oxide were added, although much more could have been reacted.

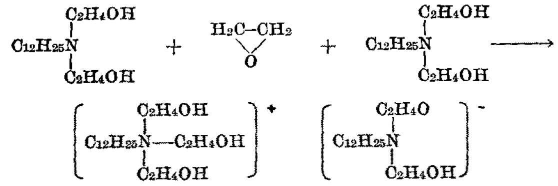
The final product would be expected to contain mainly ethoxylated butanol and unreacted dimethyl lauryl amine. There should be little or no free butanol present. If quaternary ammonium butoxide is formed during the reaction, its decomposition by heating should give butanol. To test this, the product was analyzed before and after heating.

Thus, a 5 μliter sample was passed through the gas chromatograph, using an Apiezon L column (2 ft × 0.25 in.) with an oven temperature of 85 C, injection temperature of 85 C and detector at 95 C. Chart speed 0.5 in./min.

Analysis of the peaks showed a butanol content of 0.6% (Fig. 5, left hand). A second sample was then heated at 110 C for 30 min and chromatographed as before (Fig. 5, right hand); this time 3.0% of butanol was found, confirming the expected increase.

It should be mentioned that the butoxide anion can also be ethoxylated during addition of ethylene oxide, hence only part of the quaternary anion is butoxide, the rest being $RO(C_2H_4O)_n^-$.

In light of the preceding results, the theory that the free base formed during amine ethoxylation is generated by water split off from alkyl morpholine was reconsidered. It is conceivable that the base could be a quaternary ammonium alcoholate rather than hydroxide, being formed as follows:



This quaternary would not require water for formation, and it is believed this route probably may account for most of the free base observed, with perhaps a minor amount coming from morpholine dehydration.

A brief excursion was also made into a study of fatty amide ethoxylations as part of this work. Thus lauramide, $C_{11}H_{23}CONH_2$ (Armid C, Armour Industrial Chemical Co., Chicago) was treated for long periods with ethylene oxide at temperatures from 100–150 C, but no reaction took place in the absence of added catalyst. No free base was formed under these conditions. Apparently the carbonyl group inhibits reactivity of the $-NH_2$ with ethylene oxide.

The ethoxylation of lauryl monoethanolamide ($C_{11}H_{23}CONHC_2H_4OH$) was also investigated to determine whether the carbonyl influence would also be evident here. Monoethanolamides made with a slight excess of monoethanolamine, as is the usual practice, reacted readily with the ethylene oxide at 100 C. However, large amounts of free base formed during the reaction. It was assumed this was produced from the excess monoethanolamine present. Hence a portion of the lauryl monoethanolamide was vacuum stripped at 130 C and 10 mm Hg to reduce the monoethanolamine from about 5% to 0.2%. This time it was found that ethylene oxide did not add to the amide at temperatures from 100–150 C, and no free base was detected.

It therefore appears that pure lauryl monoethanolamide cannot be ethoxylated in the absence of added catalysts.

REFERENCES

1. Schick, M. J., editor, "Nonionic Surfactants," Marcel Dekker, Inc., New York, 1967.
2. Shapiro, "Fatty Acids and Their Application," E. S. Pattison, editor, Marcel Dekker, Inc., New York, 1968, p. 141.
3. Komori, S., S. Sakakibara and A. Fujiwara, Tech. Rept. Osaka Univ. *6*, 387 (1956).
4. Komori, S., and T. Karaki, Ibid. *10*, 249 (1960).
5. Ulrich, H., and E. Ploetz, U.S. Patent 2,127,476 (1938).
6. Reck, R. A., U.S. Patent 2,597,260 (1952).

[Received October 9, 1968]