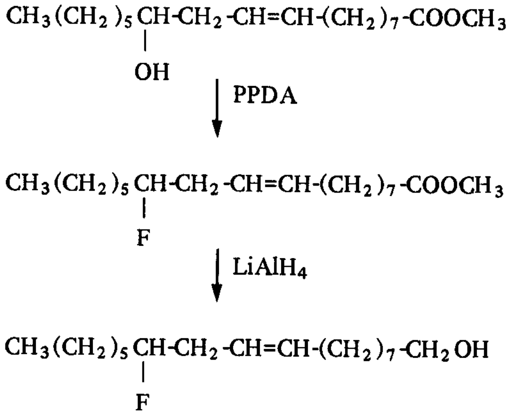
J=8.0Hz, $-CH_2COOCH_3$), 3.44 (3H, s, $-COOCH_3$), 4.52 (1H, dm, J=44.0Hz, -C$\underline{H}$F-); ^{19}F NMR (δ, ppm) ($CDCl_3$); signal of F (multiplet) was recognized at 99 upfield from the external standard of CF_3COOH. Compound (IV) showed ions at m/e 296 (M±HF) and m/e 264 (M±HF-CH_3OH) in its mass spectrum.

Reduction of Methyl 12-Fluoro-9-octadecenoate (II) with Lithium Aluminum Hydride

A solution of compound (II) (0.3 g) in dry diethyl ether (30 ml) was dropped into a suspension of lithium aluminum hydride (0.2 g) in dry diethyl ether (30 ml) at 0 C. After stirring for 5 hr, the reaction mixture was decomposed by adding 1% hydrochloric acid. It was extracted with diethylether. The ether extract was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to remove the solvent. The residue was chromatographed with silica gel column using n-hexane containing ethyl acetate (1%) as a solvent. From the elution, 0.1 g of 12-fluoro-9-octadecenol (III) was obtained. It showed the following properties. Ir (cm^{-1}): 3200, 1640, 1058, 720; NMR (δ, ppm): 0.98 (3H, t, J=5.0Hz, CH_3-), 1.28 (20H, s, $-CH_2$-), 1.70-2.60 (8H, m, other $-CH_2$-), 3.50 (1H, s, -O$\underline{H}$), 4.43 (1H, dm, -CHF-), 5.35 (2H, m, -CH=CH-); ^{19}F NMR (δ, ppm) ($CDCl_3$): signal of F (multiplet) was recognized at 98.5 upfield from the external standard of CF_3COOH.

RESULTS AND DISCUSSION

We have reported that PPDA can be applied for fluorination of primary fatty alcohols and various glycerol derivatives (1,2). However, fluorination of standard secondary alcohols with PPDA gave a mixture of fluoride, a dehydration product and a dimeric ether. On trial, the fluorination of methyl ricinolate (I) with PPDA was examined. The use of an excess of dichloromethane as a solvent is the best condition for its preparation of the fluoride (II), which was obtained in 61% yield. II was purified by molecular distillation; in thin layer chromatography it showed a single spot. The structure of II was determined by the spectral data of IR, ^{1}H NMR, ^{19}F NMR and MS. Reduction of II with lithium aluminum hydride gave 12-fluoro-9-octadecenol (III). Biochemical investigation of these fluorides is now in progress at our laboratory.



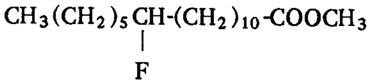
$$CH_3(CH_2)_5\underset{OH}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOCH_3 \qquad (I)$$

$$\Big\downarrow \text{PPDA}$$

$$CH_3(CH_2)_5\underset{F}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOCH_3 \qquad (II)$$

$$\Big\downarrow \text{LiAlH}_4$$

$$CH_3(CH_2)_5\underset{F}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2OH \qquad (III)$$



$$CH_3(CH_2)_5\underset{F}{CH}\text{-}(CH_2)_{10}\text{-}COOCH_3 \qquad (IV)$$

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N. Ishikawa and T. Kitazume of the Tokyo Institute of Technology provided guidance throughout this work and the measurements of ^{19}F NMR spectra.

REFERENCES

1. Watanabe, S., T. Fujita, K. Suga and I. Nasuno, JAOCS, 60:1678 (1983).
2. Watanabe, S., T. Fujita, I. Nasuno and K. Suga, JAOCS 61:1479 (1984).

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*Catalytic Effect of Amines on the Ethoxylation of Dodecyl Alcohol

PÉTER SALLAY, JENÖ MORGÓS, LÁSZLÓ FARKAS, ISTVÁN RUSZNÁK, GÁBOR VERESS and **BÉLA BARTHA**, Department of Organic Chemical Technology,
Polytechnical University of Budapest, PO Box 91, H-1502 Budapest, Müegyetem,
Hungary

ABSTRACT

The catalytic activity of several tertiary amines on the ethoxylation of dodecyl alcohol has been investigated. It has been established that the rate of the reaction is proportional to the concentration of the catalyst over the range of 10-25% and that the reaction rate has an extremum at 80 C.

The catalytic effect of trialkyl amines increases if two of the alkyl groups are methyl. The product distribution is that of the Weibull-Nycander-Gold type and is independent of the concentration of the catalyst and reaction temperature. Distribution constants calculated according to Natta-Mantica vary with the average degree of ethoxylation, i.e., the Weibull-Törnquist effect is observed. This can be explained if an interaction is assumed between the polyethylene glycol chain formed and the quaternary ammonium ion formed in the first step of ethoxylation.

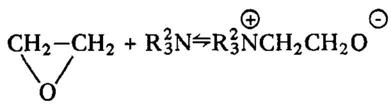
INTRODUCTION

The ethoxylation of dodecyl alcohol has been reported previously (1). The reaction is catalyzed by alkali hydroxides at temperatures above 100 C, except in cases when special additives are used (2). These conditions cause some difficulties, since an increase in reaction temperature can result in the discoloration of the product. Thus, an attempt was made to catalyze the ethoxylation with amine catalyst, so as to allow the reaction to proceed at a lower reaction temperature.

The ethoxylation of fatty alcohols also can be carried out with an amine catalyst. In some cases primary or secondary amines are used (3), and the amine is also ethoxylated. However, tertiary amines generally are used as catalysts (4, 5, 6, 7).

Under amine catalysis the mechanism of the reaction is different from that of catalysis by alkali hydroxides.

Tertiary amine catalysis is a two-stage process (7): the first reaction, between the amine and ethylene oxide, leads to a quaternary ammonium zwitterion



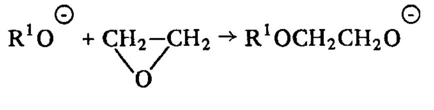
[eq. 1]

This zwitterion undergoes rapid equilibration with the alcohol to be ethoxylated so as to yield the alcoholate anion shown in eq. 2.

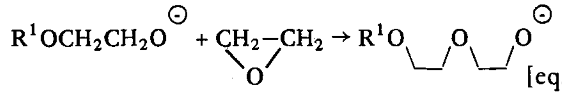
$$R^2_3\overset{\oplus}{N}CH_2CH_2\overset{\ominus}{O} + R^1OH \rightleftharpoons R^2_3\overset{\oplus}{N}CH_2CH_2OH + R^1\overset{\ominus}{O}$$

[eq. 2]

From this point, the reaction is similar to the reaction catalyzed by sodium alkoxide in that the alcoholate anion reacts with the ethylene oxide in a chain elongation process.



[eq. 3]



[eq. 4]

In the ethoxylation of mercaptanes the effective catalyst has a similar structure (8)

$$R_3\overset{\oplus}{N}CH_2CH_2OH\cdot R\overset{\ominus}{S}$$

The effect of hydroxy groups of the substrate and product on the oxygen of ethylene oxide also should be taken into account (4, 8), because increased temperature does not favor the reaction (4).

There is little information available on the distribution of products formed in the amine catalyzed reactions. From the distribution constants given by Stockburger and Brandner (5), a distribution of homologues of the Weibull-Nycender-Gold type ($c \sim 3$) can be concluded.

EXPERIMENTAL

Ethoxylation reactions, gas chromatographic analysis of products and calculation of distribution constants (c, c_i) were carried out as described earlier (1).

Materials used were dodecyl alcohol ("Alfol 12," Condea); tributyl amine (Hoechst); trioctyl amine (Hoechst); N-butyl-ethanol amine (Fluka), and pyridine (Reanal).

N-N-dimethyl octyl amine and N-N-dimethyl-butyl amine were synthesized from octyl amine and butyl amine (Hoechst) according to the Leuckart-Wallach reaction (9).

RESULTS AND DISCUSSION

Ethylene oxide consumption was followed as a function of reaction time (Fig. 1). The average degree of ethoxylation (v = amount of ethylene oxide reacted per 1 mole of the starting material in moles) as a function of time provided straight lines for each amine studied. The correlation coefficients were between 0.985 and 0.999. The slopes were taken as initial reaction rates ($w = v/t$). The ethoxylation rates obtained with several different amine catalysts are summarized in Table I.

It is seen that tertiary aromatic amines (pyridine, dimethyl aniline) do not catalyze the reaction, whereas tertiary alkyl amines are good catalysts over the concentration range of 10-25%.

The reaction of more reactive alcohols (e.g., methyl alcohol) with ethylene oxide, however, has been catalyzed with dimethyl aniline (7). In the case of triethyl amine the low boiling point of the catalyst results in a high loss during the reaction. Therefore, this was omitted from this study.

The lower activity of trioctyl amine relative to tributylamine and of both amines to the dimethyl derivatives can be explained on the basis of the reaction pathway. In the

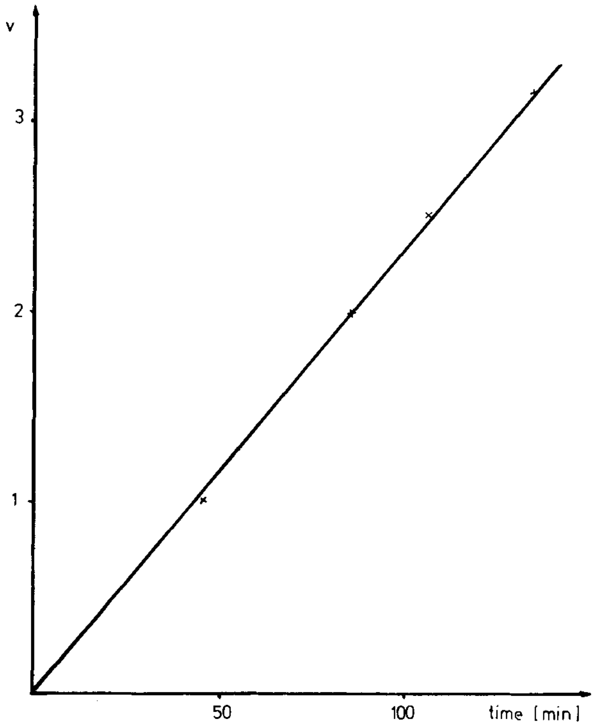


FIG. 1. Rate of ethoxylation with tributyl amine as catalyst (at 80 C, 15%).

TABLE I

Ethoxylation Rates Obtained with Different Catalysts at 80 C

Amine	w X 10² (mol/mol. min)			
	10%[a]	15%[a]	20%[a]	25%[a]
Tributyl amine	2.04	2.29	2.58	2.85
Trioctyl amine	–	1.86	2.01	2.22
Dimethyl-butyl amine	–	4.81	5.73	–
Dimethyl-octyl amine	42.7	4.97	5.80	–
N-butyl-ethanol amine	1.64	1.91	2.29	–
N,N,N,N-tetramethyl-ethylene diamine	–	4.45	–	–
Dimethyl-aniline	–	0	0	0
Pyridine	–	0	0	0

[a]The percentage of amine refers to mol amine per mole alcohol.

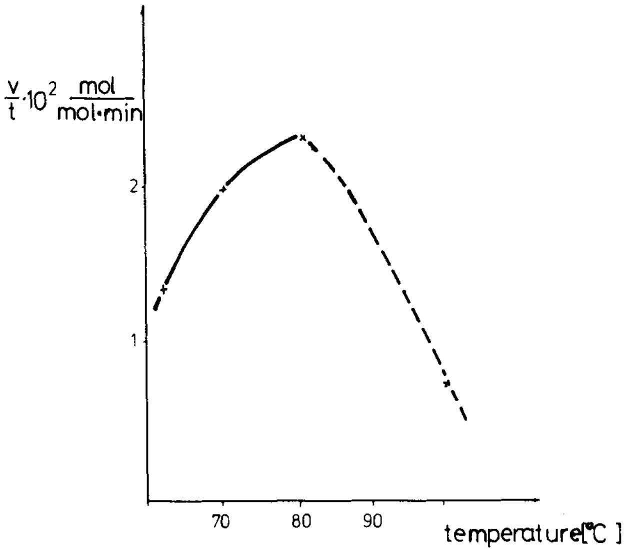


FIG. 2. Variation in the rate of ethoxylation as a function of temperature (tributyl amine, 15%).

TABLE II

Dependence of Reaction Rate on Catalyst Concentration at 80 C ($w = a\ c_a + b$)

Amine	Proportionality coefficient[a] ($w/c_a \times 10^4$)	Correlation coefficient r
Tributyl amine	5.43	0.999
Trioctyl amine	4.75	0.999
Dimethyl-octyl amine	17.05	0.9995
N-butyl-ethanol amine	6.52	0.994

a = Proportionality coefficient; c_a = concentration of catalyst.

first step [eq. 1] the equilibrium favors the reactants over the products because of the steric hindrance of the larger alkyl groups. Consequently the concentration of active species is higher in the case of smaller alkyl chains, shown in eq. 3. Therefore, the reaction is faster.

Figure 2 shows that the rate of the reaction catalyzed by tributyl amine has a maximum of 80 C similar to the data given by Oshiro, Ochiai and Komori (4). This probably is due to the thermal instability of the quaternary ammonium ion. (According to Laird and Parker (7), the quaternary ammonium hydroxide is stable below 60 C). Hence, the two steps of ethoxylation consist of two processes which depend differently on the temperature of the reaction. With increasing temperature the equilibrium reaction for quaternization decreases [eq. 1], whereas the reaction rate of alkoxyde ion with ethylene oxyde [eq. 3] increases. The optimum reaction temperature is about 80 C.

We also have found that the reaction rate is proportional to the concentration of the catalyst over the concentration range studied (Table II). Linear relationships, however, have been obtained only at relatively high concentrations of the catalyst.

In each case, the distribution of products was of the Weibull-Nycander-Gold type. This means that a graph of x_i versus v has two extreme values and the distribution coefficient [c by Weibull, Nycander (10) and Gold (11)] greater than one. This is shown in Figure 3 for tributyl amine, trioctyl amine and N,N-dimethyl-octyl amine, and the results are compared with those calculated by Flory (12) and Weibull-Nycander-Gold distributions. The measured distribution agrees satisfactorily with the theoretical Weibull-Nycander-Gold distribution, and only for higher homologues (i=4) are the deviations significant. (For N-butyl-ethanol amine the distribution also is of this type, and the larger deviation is due to the ethoxylation of the catalyst.)

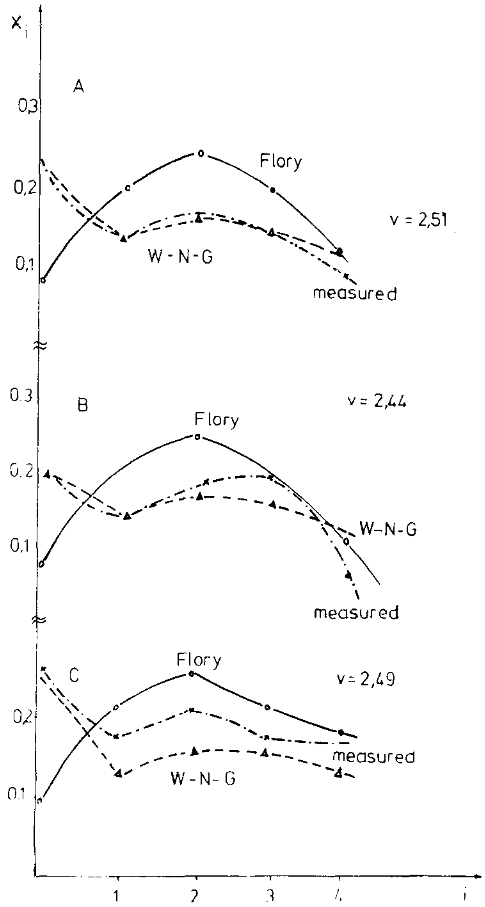


FIG. 3. Distribution of the reaction products with tributyl amine (A), with trioctyl amine (B), with dimethyl amine (C) as catalyst.

It also has been established that the product distribution is independent of the concentration of the catalyst, i.e., the relative scatter of mole fractions is smaller than the experimental error. A change in temperature did not cause a significant difference in the distribution.

Distribution constants also have been calculated according to Natta-Mantica (13) and the numerical values for tributyl, trioctyl and N,N-dimethyl-octyl amine are summarized in Table III. Their graphic representation is given in Figure 4 for trioctyl amine. The curves are similar to those for the other amines investigated.

From these results it is apparent that the distribution constants are not real constants, since they vary with the average degree of ethoxylation.

Thus the Weibull-Törnquist effect (15) shown by us for alkali hydroxides (1, 14) i.e., that the distribution constants are a function of the degree of ethoxylation, is also valid for reactions catalyzed by amines.

The reason for this is the same as suggested for alkali hydroxydes (1, 14). The counterion of alcoholate

$$(R_3\overset{\oplus}{N}-CH_2CH_2OH)$$

can form a complex with the oligoethylene glycol chain produced (a crown ether-like effect) as has been shown for

TABLE III

Dependence of Distribution Coefficients on the Average Degree of Ethoxylation (v), at 80 C, Concentration of Catalyst 15%, Variance ± 0.05

Amine	v	c	c_1	c_2	c_3	c_4
Tributyl amine	3.13	2.82	2.46	2.18	1.93	1.43
	2.51	2.40	2.37	2.11	1.86	1.56
	1.98	2.32	2.22	2.14	2.12	1.97
	1.01	1.03	2.27	2.91	5.74	9.65
Trioctyl amine	2.70	2.39	2.17	1.89	1.06	2.47
	2.44	2.26	2.31	1.99	1.31	3.14
	2.09	2.43	2.18	2.22	1.53	4.39
	1.45	2.39	2.18	2.87	2.05	>50
	0.94	2.27	2.60	4.09	4.22	38.8
	0.45	2.22	3.79	7.29	19.74	>50
Dimethyl-octyl amine	2.49	2.80	2.19	1.94	1.85	0.26
	1.98	1.90	1.99	2.05	1.99	0.79
	1.47	1.58	1.89	2.39	1.78	1.05
	1.08	2.01	2.24	2.78	2.51	1.90

c = Distribution coefficient according to Weibull-Nycander-Gold (10, 11).
c_i = Distribution coefficients according to Natta-Mattica (13).

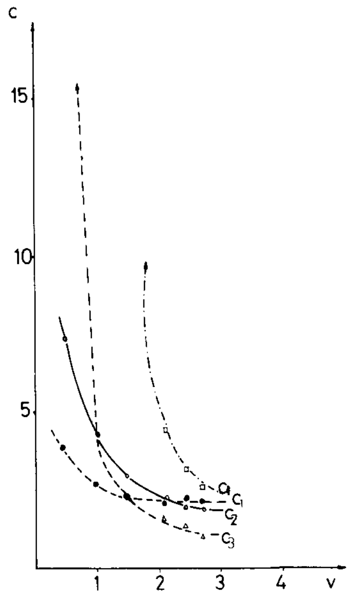


FIG. 4. Variation of distribution constants with trioctyl amine catalyst.

other ammonium ions (16). This effect can also be observed when the ethoxylated chain is long enough to form complex with the anion. In this case the relative rates change and by this means the distribution coefficients too. The more symmetrical is the ammonium ion the more is the effect of the glycol chain.

REFERENCES

1. Farkas, L., J. Morgós, P. Sallay, I. Rusznák, B. Bartha and G. Veress, JAOCS 58:650 (1981).
2. Morgós, J., P. Sallay, L. Farkas and I. Rusznák, JAOCS 60: 1905 (1983).
3. Bartha, B., Tenside Detergents 10:302 (1973).
4. Oshiro, Y., M. Ochiai and S. Komori, Kogio Kagaku Zasshi 64: 1588 (1961).
5. Stockburger, G.J., and D. Brandner, JAOCS 40:590 (1963).
6. Jap. Pat: 81 15, 229 (1981).
7. Laird, R.M., and R.E. Parker, J. Chem. Soc. B. 1969:1062.
8. Shvets, V.F., Yu Likov and A.R. Kugel, Kinet. Katal. 16:639 (1975).
9. Moore, M.L., Org. Reactions 5:301 (1949).
10. Weibull, B., and B. Nycander, Acta Chem. Scand. 8:847 (1954).
11. Gold, L., J. Chem. Phys. 28:91 (1958).
12. Flory, P.J., J. Am. Chem. Soc. 62:1561 (1940).
13. Natta, G., and E. Mantica, Ibid. 74:3152 (1952).
14. Sallay, P., J. Morgós, L. Farkas, I. Rusznák, G. Veress and B. Bartha, Tenside Detergents 17:298 (1980).
15. Weibull, B., and J. Törnquist, in "Chemie, Physikalische Chemie und Anwendungstechnik der Grenzflächenaktiven Stoffe," Carl Hanser Verlag, München, 1973, p. 125.
16. Rashofer, W., and F. Vögtle, Tetrahedron Letters 1978:309.

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