The Chemistry of "Alfol"[1] Alcohols

MARK T. ATWOOD, Continental Oil Company, Ponca City, Oklahoma

Abstract

The Continental Oil Co. has developed a process for producing straight chain, primary alcohols from petrochemical sources. These alcohols may be converted into a variety of derivatives possessing a wide range of use properties.

Introduction

Straight chain primary alcohols have been produced from animal fats and vegetable oils for many years. These products have found wide use in the detergent, plasticizer, and other industries. Continental Oil Co. has recently placed on stream, a large plant designed to produce a series of straight chain alcohols ranging from ethanol to eicosanol ($C_{20}H_{41}OH$). These products bear the tradename "ALFOL" alcohols. The "ALFOL" plant, at Lake Charles, La., utilizes aluminum, ethylene, hydrogen, and air as raw materials and has a total capacity of 100 million lb per year.

The "ALFOL" process has been thoroughly discussed elsewhere (1). In brief, the process involves the reaction of metallic aluminum with hydrogen and two moles of aluminum triethyl to give three moles of diethylaluminum hydride. Reaction of the diethylaluminum hydride with ethylene gives three moles of aluminum triethyl, two of which are recycled to the first step. Aluminum triethyl is then reacted with ethylene to give a mixture of high mol wt aluminum alkyls containing randomly distributed alkyl groups. This "growth" product is then oxidized with air and hydrolyzed with water to give the "ALFOL" alcohols and aluminum hydroxide. The latter product is of potentially great value because of its high purity.

The distribution of straight chain alcohols from the "ALFOL" process is governed by the Poisson mathematical relationship. In Table I, a typical "ALFOL" alcohol distribution compared with similar distributions based on coconut oil and tallow is shown. The "ALFOL" alcohol distribution can be easily shifted to a higher or lower "peak" by adjusting reaction conditions. This "ALFOL" alcohol distribution is thus quite flexible and is especially advantageous in that "ALFOL" 14, myristyl alcohol, is now more readily available. Blends of straight chain alcohols, not previously available, can now be obtained.

The lower alcohols, "ALFOL" 6 to "ALFOL" 10, are currently being used in the manufacture of phthalate and adipate esters for use as plasticizers. When straight chain alcohols are used instead of branch chain alcohols in this application, the products have better placticizing efficiency, less volatility, more resistance to oxidative degradation, better low temp flexibility, and lower plastisol viscosity (2).

The higher alcohols, "ALFOL" 12 to "ALFOL" 20, currently find their greatest use in the manufacture of synthetic, biodegradable detergents. Three general types are in use: a) alcohol sulfates, b) alcohol ethoxylates, c) alcohol ether sulfates. These products have been described in previous publications (3, 4) and account for a major portion of the total "ALFOL" plant production.

The "ALFOL" alcohols offer commercial promise for the production of a number of other useful derivatives due to their price stability and high purity.

ALYKL CHLORIDES

The "ALFOL" alcohols may be reacted with hydrogen chloride gas in the presence of 1% zinc chloride to give a 90% yield of the primary alkyl halide.

$$[1] \qquad C_{12}H_{25}OH + HCl \xrightarrow[160C]{ZnCl_2} C_{12}H_{25}Cl + H_2O$$

The reaction is complete when water evolution ceases. Dialkyl ether is formed as the major by-product (6–8% yield), but it can be reacted with hydrogen chloride, under the same conditions used for the alcohol, to give two moles of alkyl chloride.

These higher alkyl chlorides may be reacted with sodium hydrosulfide in methanol solution to give straight chain mercaptans in yields of 85% or better (5,6).

$$[2] \qquad C_{12}H_{25}Cl + NaSH \longrightarrow C_{12}H_{25}SH + NaCl$$

The alcohol sulfate salts may be similarly converted to mercaptans (7).

$$[3] \qquad C_{12}H_{25}OSO_3M + NaSH \longrightarrow C_{12}H_{25}SH + NaMSO_4$$

n-Dodecyl mercaptan is used as a polymerization modifier in the synthetic rubber industry.

At least two ethoxylates of mercaptans are produced commercially for use in grease cutting, industrial cleaning, and metal processing.

The alkyl chlorides can be converted to nitriles by reaction with sodium cyanide in dimethyl sulfoxide. From n-decyl chloride, 1-cyanodecane was obtained in 94% yield (8).

$$[4] \qquad C_{10}H_{21}Cl + NaCN \xrightarrow{DMSO} C_{10}H_{21}CN + NaCl$$

These products may be used as plasticizers and softening agents for synthetic rubber.

ALIPHATIC AMINES

Aliphatic amines may be produced from straight chain alcohols by two general procedures. The alcohol may be directly reacted with ammonia or amines at high temp and pressure, or the alcohol may be first converted to the chloride and then reacted with ammonia or amines under more moderate conditions.

Cetyl alcohol was reacted with excess ammonia at 2000 psi and 400C to give the primary amine in 94% yield (9). Under similar conditions n-dodecyl alcohol was reacted with dimethyl amine to give dimethyl dodecyl amine in 90% yield (10).

TABLE I

Straight Chain Alcohol Distributions (wt %)

Carbon No.	"ALFOL"	Coconut Oil	Tallow
2	0.4	....	....
4	3	....	....
6	9	1	....
8	16	8	....
10	20	8	....
12	19	47	....
14	15	19	2
16	9	8	24
18	5	9	74
20	3	....	....

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[1] Registered trademark of Continental Oil Company.

[5] $C_{16}H_{33}OH + NH_3 \xrightarrow{Al_2O_3} C_{16}H_{33}NH_2 + H_2O$

[6] $C_{12}H_{25}OH + HN(CH_3)_2 \xrightarrow{Al_2O_3} C_{12}H_{25}N(CH_3)_2 + H_2O$

A more convenient route to these compounds involves the use of the alkyl chlorides. The following reactions may be carried out at around 150C and pressures below 100 psi (11):

[7] $C_{12}H_{25}Cl + NH_3 \longrightarrow (C_{12}H_{25})_2NH$ (85%)

[8] $C_{16}H_{33}Cl + CH_3NH_2 \longrightarrow (C_{16}H_{33})_2NCH_3$ (68%) + $C_{16}H_{33}NHCH_3$ (15%)

[9] $C_{16}H_{33}Cl + (CH_3)_2NH \longrightarrow C_{16}H_{33}N(CH_3)_2$ (83%)

[10] $C_{12}H_{25}Cl + (C_2H_5)_2NH \longrightarrow C_{12}H_{25}N(C_2H_5)_2$ (86%)

These amines may be used as such or may be converted to quaternary ammonium salts, amine oxides, and ethylene oxide adducts.

QUATERNARY AMMONIUM SALTS

Quaternary ammonium salts may be prepared directly from the alkyl chlorides using a limited number of tertiary amines (11). Cetyl chloride will react with trimethyl amine to give the quaternary compound in essentially quantitative yield.

[11] $C_{16}H_{33}Cl + N(CH_3)_3 \longrightarrow C_{16}H_{33}N(CH_3)_3^+Cl^-$

Dimethyl benzyl amine reacts similarly to give a dimethyl benzyl quaternary compound. In these quaternary forming reactions, the rate is somewhat low due to necessity of keeping the reaction temp below 110C.

Alkyl chlorides may be reacted directly with pyridine to give the corresponding pyridinium salts (28). The use of a solvent, such as methanol, should aid this reaction.

Quaternary compounds may also be prepared by reacting methyl chloride or benzyl chloride with the products from reactions [7–10] above.

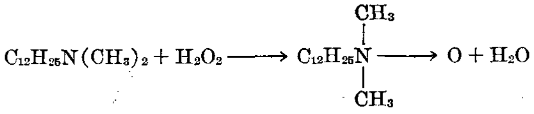
These compounds are currently being used as corrosion inhibitors, bactericides, emulsifiers, anti-static agents, dyeing aids, and textile softeners.

This last application, textile softeners, is consuming a large volume of quaternary salts and is rapidly growing as consumer acceptance becomes more general (12). The quaternary salt most used in this application is characterized by the general formula, $R_2N(CH_3)_2^+X^-$, where R is tallow derived and X^- is chloride or sulfate. This product can be prepared cheaply and in high purity by utilizing a mixture of straight chain alcohols containing 16 and 18 carbon atoms in reaction [1] above to produce the mixed chlorides followed by reactions [7] or [8] above to produce the proper amine structure. A final quaternization step with methyl chloride will then give the desired product. By adjusting the ratio of the two straight chain alcohols used in the manufacturing process it may be possible to overcome the rewetting problem which is of some concern to textile softener manufacturers.

AMINE OXIDES

Amine oxides have recently become prominent as surface active agents primarily for use as foam boosters. These products may be produced simply in high yield by reacting dimethylalkyl amine (from reaction [9] above) with 35% hydrogen peroxide (29).

[12]



$$C_{12}H_{25}N(CH_3)_2 + H_2O_2 \longrightarrow C_{12}H_{25}\underset{CH_3}{\overset{CH_3}{N}} \longrightarrow O + H_2O$$

The products are white, hygroscopic solids which are generally handled in aqueous solution.

There are at least two issued U. S. patents (13,14) on the use of amine oxides. The first patent refers to the use of amine oxides in a "personal use detergent lotion." A typical formulation includes a coconut glyceryl ether sulfonate, a tallow glyceryl ether sulfonate, lauryl dimethyl amine oxide, potassium pyrophosphate, sodium toluene sulfonate and other minor ingredients. The second patent refers to a formulation of lauryl dimethyl amine oxide with an alkali metal ethylene diamine tetraacetate. It is indicated that amine oxides, when incorporated in detergent formulations, lessen skin irritation (16). Foreign patents have also been issued concerning detergent formulations containing amine oxides (15,16).

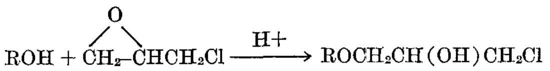
The amine oxides of the type shown above are completely biodegradable.

Patents have been issued on the use of amine oxides in latex frothing for the production of foamed rubber (17), as polymerization inhibitors (18,19), polymer light stabilizer (20), and as a pour point depressor in distillate stocks (21).

ALKYL GLYCERYL ETHER SULFONATES

The alkyl glyceryl ether sulfonates are useful detergent materials and may be prepared by the following reactions using straight chain alcohols (22):

[13]



$$ROH + \overset{O}{CH_2{-}CHCH_2Cl} \xrightarrow{H+} ROCH_2CH(OH)CH_2Cl$$

[14] $ROCH_2CH(OH)CH_2Cl + Na_2SO_3 \longrightarrow ROCH_2CH(OH)CH_2SO_3Na + NaCl$

An improved process was recently patented (23).

These surface active agents are useful in detergent formulations as lathering and cleansing agents (13). They possess good solubility in cold water and are stable in the presence of acids, lime, and magnesium salts.

CARBOXYLIC ACIDS

Straight chain alcohols may be reacted with molar amounts of caustic to give the corresponding carboxylic acids in high yields (24).

[15] $C_{12}H_{25}OH + NaOH \xrightarrow{270C} C_{11}H_{23}CO_2H$

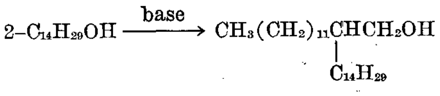
Caustic oxidation appears to be attractive for the production of higher acids from "ALFOL" 20 and "ALFOL" 20+. "ALFOL" 20, "ALFOL" 22, and "ALFOL" 24 have been converted to the corresponding acids in 95–98% yields (27).

These higher acids may have utility in cosmetics, emulsifiers, specialty coatings, plasticizers, synthetic waxes, and water repellent formulations for textiles.

DIMER ALCOHOLS

Straight chain alcohols may be subjected to the well known Guerbet reaction to give a branched alcohol containing twice the original number of carbon atoms (25,26).

[16]



$$2{-}C_{14}H_{29}OH \xrightarrow{base} CH_3(CH_2)_{11}\underset{C_{14}H_{29}}{CH}CH_2OH$$

This reaction offers a straightforward route to higher alcohols, e.g., C_{24} to C_{40}. No known uses exist for these compounds since they have generally not been available.

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[Received September 13, 1962—Accepted October 23, 1962]

Foaming Properties of Nonionic Detergents[1]

M. J. SCHICK and E. A. BEYER, Lever Brothers Co., Research Center, Edgewater, New Jersey

Abstract

The *foam formation* and *foam stability* of aqueous solutions of polyoxyethylene tridecanols, t-octylphenols, nonylphenols, n-dodecanols, and n-octadecanols have been determined as a function of ethylene oxide chain length. In general nonionic detergents form unstable foams; the most stable foams formed by nonionic detergents are comparable to that of sodium dodecylbenzene sulfonate in the absence of foam promoters. In each homologous series of a nonionic detergent the foam formation and foam stability pass through a max at a critical hydrophilic-hydrophobic balance (CHHB). It is shown that the CHHB corresponds to conditions of minimum foam drainage and max resistance to film rupture.

Introduction

IN SPITE OF the expanding application of nonionic detergents, relatively few papers on their foaming properties have appeared in the literature compared to those of ionic detergents, because monodisperse materials are difficult to prepare (1,2,3). Their synthesis has been reported so far for a chain length of one to six ethylene oxide units only (4). Nonionic detergents, which have been prepared by the condensation of ethylene oxide with alkylphenols or aliphatic alcohols, yield products in which the hydrophilic portion has a Poisson distribution of chain length (5). In order to cover a wide range of molecular structures, molecularly distilled ethylene oxide condensates of alkylphenols or aliphatic alcohols have been used in this investigation of the foaming properties of nonionic detergents in aqueous solutions (6). Since in practical applications detergent solutions are mainly used at elevated temps, this investigation was carried out at 55.0C.

The principal factors determining the stability of foams have recently been reviewed by DeVries, Kitchener and Cooper, and Mysels et al. (7,8,9). The collapse of foam involves two main factors: (1) Film drainage and (2) film rupture. The foam lamella must first drain until its thickness is reduced to 50–100Å, after which it will eventually rupture. The rate of drainage is primarily dependent on the viscosity of the absorbed film. Hence, a high surface viscosity leads to a slow-draining and stable film, or vice versa. Measurements of surface viscosity or of the rate of movement of interference fringes, which has been so successful in the study of slow-draining foams of ionic detergents, were unsuccessful when applied to fast-draining foams of nonionic detergents (9,10,11), On the other hand the foam fractionation technique of Walling et al. appeared to be applicable to this study (3). The film rupture is dependent on the cohesive forces (Gibbs' elasticity) existing in the adsorbed film, whose magnitude has been deduced from the molecular configurations of nonionic detergents in adsorbed films. A detailed study of these configurations has already been reported elsewhere (6).

Experimental Procedures and Data

Materials. The ethylene oxide (EO) condensates of branched tridecanol, t-octylphenol, branched nonylphenol, n-dodecanol, and n-octadecanol have been obtained from General Aniline and Film Corp., Monsanto Chemical Co., and Rohm and Haas Co. All samples were molecularly distilled in order to remove unreacted components and reduce the width of the mol wt distribution. The average chain length of the ethylene oxide adducts was determined from their hydroxyl values, and their homogeneity was assessed from the sharp breaks in the surface tension vs. logarithm of concentration plots, which correspond to the critical micelle concentration (c.m.c.) (6). All nonionic detergents used exhibited sharp breaks. The sodium dodecylbenzene sulfonate (NaDDBS) was of 99.9% purity. Distilled water of 2×10^{-6} mho/cm specific conductance was used.

Procedures. The foaming properties were determined with a piston plunger agitator equipped with perforated disks. The stroke length was 5 in. and the stroke speed 56 cycles/min. The detergent solutions, 200 ml, were contained in covered graduated cylinders, which were thermostated at 55.0C. The foam formation is expressed as ml of foam volume generated after 15 min agitation and the foam stability as the time required for the foam volume to decay to one half of the initial height in the closed system after agitation has been halted. The foam drainage properties of 0.1% w. detergent solutions were determined by the method of Walling et al. at 55.0C (3). This procedure gives useful results primarily with rapidly draining films in which the loss of liquid from the foam occurs mainly by loss of water from the films of the intact foam lamellae. The apparatus consists of a 5 liter spherical vessel with a heating mantle, interchangeable columns of 9.4 cm i.d. and a

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[1] Paper presented in part at the 34th National Colloid Symposium, Lehigh University, Bethlehem, Pa., 1960.