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SURFACTANTS AND DETERGENTS TECHNICAL

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Technical

Synthesis and Properties of 2-Alkoxy-N, N-Dimethylethylamine N-Oxides

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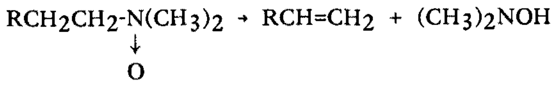
ABSTRACT

2-Alkoxy-N,N-dimethylethylamines (*1*) were prepared from the reaction of alkyl chlorides with 2-dimethylaminoethanol in the presence of potassium hydroxide. Amine oxide surfactants *2* were prepared by oxidation of *1* with hydrogen peroxide. The surfactants *2* were good foam stabilizers and stable up to 100 C, but decomposed rapidly to vinyl ethers at 150 C.

INTRODUCTION

The use of surfactants in organic synthesis to catalyze reactions between water-soluble salts and water-insoluble organic substrates has been limited, in part, by the formation of troublesome emulsions during reaction mixture work-up. Recently several research groups (1,2,3,4) have prepared some destructible surfactants that can be used for catalysis and then decomposed to nonsurfactant product prior to straightforward work-up. On the other hand, emulsion is very useful for treating water-insoluble organic compounds in aqueous phase. After application of emulsions to, for example, textiles as water-proofing agents, elimination or decomposition of the emulsifiers is more often desirable because reemulsification of the applied agents reduces the water-proofing property. Furthermore, it is desirable that destruction of the emulsifiers gives products reactive toward, for example, textiles, giving favorable properties for the textiles.

Amine oxide is one of the commercially important nonionic surfactants under neutral or alkaline conditions. Although not nearly so basic as the parent tertiary amine, they are weakly cationic in acid solutions (5). The oxides of tertiary amines decompose when heated to yield an olefin plus a derivative of hydroxylamine (Cope elimination, eq. [1] (6).



$$RCH_2CH_2\text{-}\underset{\substack{\downarrow \\ O}}{N}(CH_3)_2 \rightarrow RCH{=}CH_2 + (CH_3)_2NOH \qquad [1]$$

The effects of reaction conditions on the product distribution are thoroughly investigated, and aliphatic olefins are prepared in high yields when amine oxides are heated at 200 C, whereby the hydroxylamines produced should be removed from the pyrolysis system (7). A few examples of a low temperature decomposition of amine oxides which may be base catalyzed have been described, but the amine oxides were too labile to isolate (6).

Vinyl ethers can be prepared by a variety of methods. 2-Alkoxyethylammonium chlorides are interesting com-

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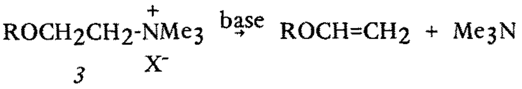
pounds as one of cationic surfactants and a precursor of vinyl ethers [eq. 2] (8).



$$\underset{3}{ROCH_2CH_2\text{-}\overset{+}{N}Me_3}\ \underset{X^-}{} \xrightarrow{base} ROCH{=}CH_2 + Me_3N \qquad [2]$$

We also prepared some of the surfactants *3* and found that *3* were rather unstable under alkaline conditions because of the Hofmann elimination reaction.

We report herein the synthesis and characterization of thermally destructible surfactants, 2-alkoxyethylamine oxides, which are stable at 100 C for extended periods and give vinyl ethers when heated up to 150 C. Vinyl ethers are well-known as one of the reactive olefins (9).

EXPERIMENTAL PROCEDURES

Materials

Alkylchlorides, 2-dimethylaminoethanol and hydrogen peroxide were the best available commercial materials and were used without further purification. All the melting and boiling points are uncorrected. NMR spectra were measured on a Varian T-60A instrument. Satisfactory analytical data were obtained for the new compounds reported here.

Etherifications and Oxidations

The preparation of 2-lauryloxy-N,N-dimethylethylamine oxide is a typical etherification and oxidation and is described as an example.

2-Dimethylaminoethanol (71g, 80ml, 0.8mol) and potassium hydroxide (15g, 0.25mol) were heated to 50 C to give a clear solution. Lauryl chloride (41g, 0.2mol) was added to the solution, and the reaction mixture was stirred and heated at 45-50 C for 72hr. The reaction flask was fitted with a condenser and side arm for collection of distillate. Heating was continued until dimethylaminoethanol ceased to be collected under vacuum (15-20mmHg). The reaction product was poured into 100ml water. The separated oil layer was collected and dried over $MgSO_4$. Distillation of it gave 2-lauryloxy-N,N-dimethylethylamine (*1e*) with contamination of a trace amount of N,N-dimethyllaurylamine. The ^1H NMR (δ, in $CDCl_3$) of *1e* shows 0.95(3H, t), 1.25(20H, m), 2.23(6H, s), 2.47(2H, t), 3.28-3.62(4H, m).

A solution of 25.7g (0.1mol) of *1e* in 100ml of acetone was cooled in an ice bath, and 17g (0.15mol) of a 30% hydrogen peroxide aqueous solution was added slowly. The solution was allowed to come to room temperature and stand overnight. The excess peroxide was decomposed by stirring the solution with 0.1g of platinum black for 6hr. The platinum black was separated and the filtrate was concentrated in a drying box under reduced pressure to give a crystalline solid. The amine oxides were recrystallized from acetone. The ^1H NMR (δ, in $CDCl_3$) of *2e* shows 0.90(3H, t) 1.25(20H, m), 3.26(6H, s), 3.30-3.63(4H, m), 3.92(2H, t).

Pyrolysis

The amine oxides *2* were heated in a nitrogen atmosphere at 10mmHg in a round-bottomed flask connected through a short cooling column to two traps in series, the first cooled with water and the second with liquid nitrogen (trapping of dimethylhydroxyamine). The flask was placed in an oil bath and heated up to 180 C. The pyrolysis was monitored using NMR absorption of methyl protons on *2* and vinyl protons on vinyl ethers. The ^1H NMR of the vinyl ethers show the same (butyl vinyl ether) or similar ones to reference compounds (12).

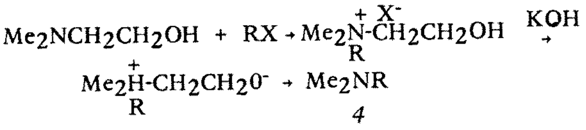
RESULTS AND DISCUSSION

2-Alkoxy-N,N-dimethylethylamines (*1*) were prepared as follows [eq. 3].

$$RX + HOCH_2CH_2NMe_2 \rightarrow \underset{1}{ROCH_2CH_2NMe_2} \qquad [3]$$

Quarternary ammonium halides were formed as a by-product, the amounts for the halide increasing in the order I > Br > Cl. Thus, special conditions were necessary to assure preparation of the expected amines. Alkyl chlorides were the best substrate, and the alkoxyethylamines were isolated in high yields (Table I).

A trace amount of N,N-dimethylalkylamines (*4*) was obtained as a by-product, probably from N-alkylation followed by internal nucleophilic substitution [eq. 4].



$$Me_2NCH_2CH_2OH + RX \rightarrow Me_2\underset{R}{\overset{+\ X^-}{N}}\text{-}CH_2CH_2OH \xrightarrow{KOH} Me_2\underset{R}{\overset{+}{N}}\text{-}CH_2CH_2O^- \rightarrow \underset{4}{Me_2NR} \qquad [4]$$

The by-product *4* increased in yield when the reaction temperature was raised, because N-alkylation is more favorable at high temperature than 0-alkylation. Other methods of ether syntheses, including aqueous-organic biphase in the presence of a phase transfer catalyst ($Bu_4N.Br$); in homogeneous solutions by use of sodium dimethylaminoethoxide; [eq. 5], and [eq. 6] (10) were rather cumbersome and gave no satisfactory results.

$$Me_2NCH_2CH_2Cl + RONa \rightarrow 1 \qquad [5]$$

$$ROCH_2CH_2Cl + Me_2NH \rightarrow 1 \qquad [6]$$

The oxidation of the amines *1* was carried out in acetone by use of aqueous hydrogen peroxide. Recrystallization of the products from acetone gave the expected crystalline amine oxides *2* in 85-95% yields (Table II). The amine oxides *2* were particularly hygroscopic and, therefore, the melting points in a sealed tube shown in Table II were not strictly those of the pure ones. An aqueous solution of the amine oxides was prepared from the reaction of aqueous suspension of the amines *1* with a 30% aqueous hydrogen peroxide solution with good agitation at 60-65 C.

Measurement of surface tension of aqueous solutions of the amine oxides at 25 C on a Du Nouy surface tensiometer gave values of 33-46mN/m and critical micelle concentration (cmc) of the amine oxides slightly lower than those of N,N-dimethylalkylamine oxides having the same hydrocarbon chain length (Table II). All the amine oxides (*2c-h*) had good foam height and were effective foam stabilizers.

Thermolysis of the amine oxides *2* was taking place at a moderate rate at 120 C and at a rapid rate at 150 C. Table III shows the thermolysis rate constants and yields of vinyl ethers heated at 150 C for 5 min. Vinyl ethers deteriorated

TABLE I

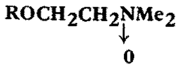
2-Alkoxy-N,N-Dimethylethylamine (*1*)^a

1	R	B.P. (°C/mmHg)	Yield(%)
a	n-C_4H_9	64/21	83
b	n-C_6H_{13}	92/23	82
c	n-C_8H_{17}	122/22	80
d	n-$C_{10}H_{21}$	97/0.6	82
e	n-$C_{12}H_{25}$	95/0.1^b	80
f	n-$C_{14}H_{29}$	149/2	78
g	n-$C_{16}H_{33}$	140/0.6	78
h	n-$C_{18}H_{37}$	175/0.6	75

[a] Satisfactory analytical data were obtained for these compounds.
[b] Lit.(7) b.p. 129/2

TABLE II

2-Alkoxy-N,N-Dimethylethylamine-N-Oxide (*2*)^a


$RO\,CH_2CH_2\underset{\overset{\downarrow}{O}}{N}Me_2$

2	R	M.P.(°C)	cmc (x 10^4,M)	Surface Tension (mN/m)
b	n-C_6H_{13}	78		
c	n-C_8H_{17}	82		
d	n-$C_{10}H_{21}$	91	8.2	46
e	n-$C_{12}H_{25}$	102	2.3	34
f	n-$C_{14}H_{29}$	79	0.46	33
g	n-$C_{16}H_{33}$	90	0.21	35
h	n-$C_{18}H_{37}$	65	0.11	36

^{a}Analytical data and ^1H NMR of these compounds show inclusion of a small amount of water.

TABLE III

Pyrolysis of the Amine Oxide *2*

2	Rate 120 C	Constant 130 C	(x 10^3,s^{-1}) 140 C	Yields (%) of Vinyl Ether^a
b	2.2	5.1	13	56
c	1.9	6.0	14	56
d	2.0	5.1	13	63
e	2.0	4.0	7.5	68
f	2.0	4.5	7.2	52
g	1.4	3.2	5.9	55
h	0.8	2.3	5.7	43

^{a}Pyrolysis of *2* at 150 C for 5 min.

in the presence of hydroxylamines, and improvement of vinyl ether yields up to 90% were accomplished by carrying out the thermolysis of *2* in reduced pressure. The rate constants were not strictly valid ones for the pure *2*, because the rate was dependent on moisture content of the amine oxides (11) and *2* are hygroscopic. Thus, complete drying of *2* was difficult. The oxides *2* with longer alkyl chain have less hygroscopic property. The smaller content of water on *2* gave the larger negative values of entropy of activation ($\Delta S^{\ddagger}$ for *2c* and *2e* were 20 and -17 e.u., respectively), suggesting intramolecular cyclic transition state of the elimination in an anhydrous state (11).

Thermal sensitivity of amine oxide surfactants has been investigated (5). At low temperatures, deoxygenation to tertiary amines is the primary reaction. Surfactants should be stable under process conditions, for example, in aqueous solutions up to 100 C.

Aqueous solutions of the amine oxides reported here were definitely stable up to 100 C. Thus, we can apply *2* as a surfactant to many processes where temperature is raised up to 100 C.

Acid-catalyzed addition of alcohols to vinyl ethers is well-known (9). Softening and water-proofing properties were imparted to cotton fabric by applying *2* and then thermolyzing them to introduce acetaldehyde acetal groups. Discoloration occurred but was minimized by treatment of the discolored materials with $NaBH_4$. Details of the application of *2* to textiles will be reported elsewhere.

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