Soap-Based Detergent Formulations: XVII. Synthesis and Surface Active Properties of Alkylbenzene Derived Amine Oxides[1]

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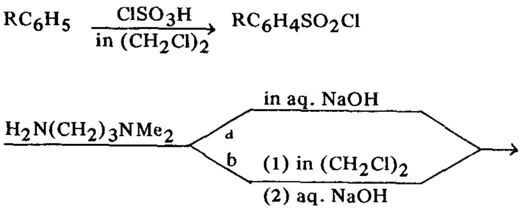
ABSTRACT

Amine oxides $C_nH_{2n+1}C_6H_4SO_2NH(CH_2)_3\overset{+}{N}Me_2—O^-$ were prepared for testing as lime soap dispersing agents in phosphate free, soap-based, sodium silicate built laundry detergents. These amine oxides were synthesized via a three step route from a variety of pure 1-phenylalkanes and also from a commercial detergent alkylate mixture. The process included (a) the sulfonation of the phenylalkane with chlorosulfonic acid, (b) reaction of the resulting alkarylsulfonyl chloride with $H_2N(CH_2)_3NMe_2$ or with $H_2N(CH_2)_3N(CH_2CH_2OH)_2$ under anhydrous conditions, and (c) oxidation with aqueous H_2O_2. The amine oxides were water soluble and in some instances isolable as crystalline hydrates. They were found to be thermally stable below 125 C and highly surface active. Optimum detergency and lime soap dispersability were achieved by the model compound of alkyl chain length n = 8. This was in contrast to the behavior of the related amphoteric sulfobetaine series $C_nH_{2n+1}C_6H_4SO_2NH(CH_2)_3\overset{+}{N}Me_2(CH_2)_3SO_3^-$, whose optimum detergency and lime soap dispersability previously had been observed to reach a maximum at chain length n = 12. Detergency screening tests showed that soap-based detergents formulated with the sulfobetaines outperformed the ones formulated with the amine oxides.

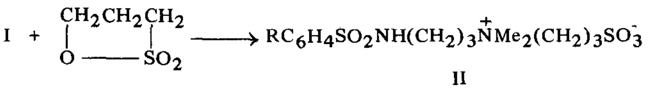
INTRODUCTION

Alkarylsulfobetaines recently have been reported to be excellent lime soap dispersing agents (LSDA) for formulation into soap-based laundry detergents (1). Their performance showed that LSDA of petrochemical origin are competitive with fat derived LSDA and can be formulated readily with tallow soap to give effective detergents (2). Their synthesis, as shown in equations [1] and [2], was based on the potentially carcinogenic (3) and commercially unavailable 1,3-propanesultone for the quaternization of the ternary nitrogen in intermediate I to the sulfobetaine II:

$$RC_6H_5 \xrightarrow[\text{in }(CH_2Cl)_2]{ClSO_3H} RC_6H_4SO_2Cl$$



$$H_2N(CH_2)_3NMe_2 \xrightarrow[\text{b: (1) in }(CH_2Cl)_2\text{; (2) aq. NaOH}]{\text{a: in aq. NaOH}} RC_6H_4SO_2NH(CH_2)_3NMe_2 \quad \text{I} \qquad [1]$$



$$\text{I} + \begin{array}{c}CH_2CH_2CH_2\\ |\qquad\quad |\\ O\text{——}SO_2\end{array} \longrightarrow RC_6H_4SO_2NH(CH_2)_3\overset{+}{N}Me_2(CH_2)_3SO_3^- \quad \text{II}$$

$$(R = C_nH_{2n+1}) \qquad [2]$$

In the present study, the ability of hydrogen peroxide to oxidize tertiary amines was utilized to form surface active amine oxides III from the above tertiary amine I, as shown in equation [3]:

$$\text{I} + 30\%\ H_2O_2 \longrightarrow RC_6H_4SO_2NH(CH_2)_3\overset{+}{N}Me_2—\overset{-}{O} \quad \text{III}$$

$$(R = C_nH_{2n+1}) \qquad [3]$$

Similarly,

$$RC_6H_4SO_2NH(CH_2)_3N(CH_2CH_2OH)_2 \ (\text{IV}) + 30\%\ H_2O_2 \longrightarrow$$

$$RC_6H_4SO_2NH(CH_2)_3\overset{+}{N}(CH_2CH_2OH)_2—\overset{-}{O} \quad \text{V} \qquad [4]$$

Such amine oxides may be viewed as amphoteric surfactants, though they differ considerably from the sulfobetaines II insofar as the distances between the oppositely charged atoms are concerned.

Long chain amine oxides of the type $R\overset{+}{N}Me_2—\overset{-}{O}$ and $RCONHCH_2CH_2CH_2\overset{+}{N}Me_2—\overset{-}{O}$ have been commercial products for some time, finding use in shampoos and hair dressings and as foam stabilizers for liquid detergents. However, aromatic amine oxides of the type III and V so far have not been reported. Both the commercial amine oxides and those of this study have been subjected to detergency screening tests to compare their performances to each other, to the sulfobetaines, and to a control high phosphate built commercial laundry detergent.

EXPERIMENTAL PROCEDURES

Materials

The following amine oxides were supplied by Onyx Chemical Co. (Jersey City, NJ): Ammonyx LO and SO ($R\overset{+}{N}Me_2—\overset{-}{O}$; R = $C_{12}H_{25}$ and $C_{18}H_{37}$, respectively); Ammonyx CDO and TDO ($RCONHCH_2CH_2CH_2\overset{+}{N}Me_2—\overset{-}{O}$; R = $C_{11}H_{23}$ and $C_{17}H_{35}$, respectively). Model compound 1-phenylalkanes were obtained from Aldrich Chemical Co. (Milwaukee, WI). Nalkylene 500 detergent alkylate mixture (average mol wt 236) was obtained from Continental Oil Co. (Ponca City, OK). Chlorosulfonic acid was the product of Matheson, Coleman, and Bell (Norwood, OH). N,N-Dimethyl-1,3-propanediamine ("Dimethylaminopropylamine") and N,N-bis(2-hydroxyethyl)-1,3-propanediamine ("N-Aminopropyldiethanolamine") were supplied by Jefferson Chemical Co. Inc. (Houston, TX).

Synthesis

Amine precursors (I): Typically, a 500 ml three neck flask was equipped with a thermometer, drying tube filled with Drierite, a 125 ml addition funnel, a magnetic stirring assembly, and an ice water bath. Adequate ventilation or a trap assembly for evolved hydrogen chloride gas was required. The flask was charged with Nalkylene 500 phenylalkane mixture (102 g, 0.432 mol) and 1,2-dichloroethane (100 ml), and the temperature was allowed to fall to

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[1] Presented at the AOCS Meeting, Dallas, April 1975.

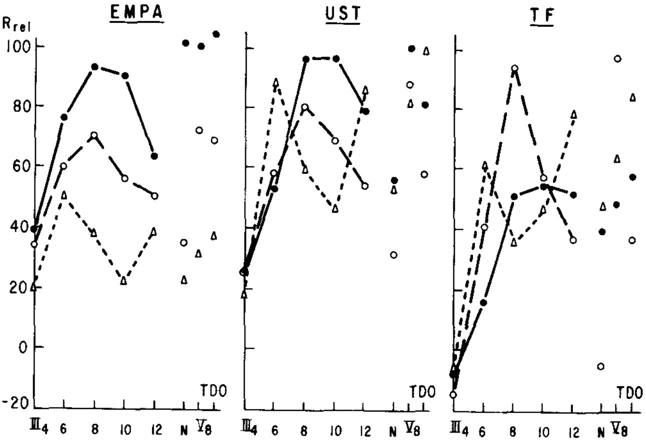

FIG. 1. Relative detergency of amine oxides (ΔR_{rel}; commercial high phosphate built detergent = 100). Conditions: 1 liter, 300 ppm hardness, 120 F, 100 rpm, 0.20% formulation, 0.002% cmc. Formulations: (Δ) = 100% amine oxide; (○) = 25% amine oxide and 75% soap; (●) = 21% amine oxide, 64% soap, and 15% silicate (SiO_2: Na_2O = 1.6). Amine oxides: III_4 = III, n = 4; III_N = III, derived from Nalkylene 500; etc. TDO = Ammonyx TDO. Standard soiled fabrics (five swatches of each per bucket): EMPA 101 (distributed by Testfabrics Inc., Middlesex, NJ) and UST (U.S. Testing Co., Hoboken, NJ) cottons and TF (Testfabrics) cotton-polyester with permanent press finish.

8-10 C, where it was maintained during the sulfonation. The addition funnel then was charged with chlorosulfonic acid (68 ml, 1.04 mol), which subsequently was added dropwise to the stirred contents of the flask. On completion of the addition, the contents were transferred to a separatory funnel equipped with a Drierite-filled drying tube. The contents separated into two layers overnight. The lower layer (chlorosulfonic and sulfuric acids) was removed and then cautiously destroyed in aqueous acetone. The solution remaining in the separatory funnel (containing the arenesulfonyl chloride) was transferred to a large beaker, treated 20 min with solid sodium carbonate (caution:effervescence) to remove residual hydrogen chloride, and filtered with the aid of diatomaceous earth. Hydrated sodium carbonate proved easier to filter than the anhydrous variety. Hydrolysis at this point was minimal, as was evident from the overall yield.

The resulting solution next was added to an addition funnel mounted on a 500 ml three neck flask equipped with a mechanical stirrer, thermometer, and water bath. The flask was charged with N,N-dimethyl-1,3-propanediamine (24 g, 0.216 mol) in 1,2-dichloroethane (25 ml). The arenesulfonyl chloride solution was added dropwise to the stirred amine solution while the temperature was maintained below 30 C. Thirty min after addition had been completed, the reaction mixture was washed with aqueous sodium carbonate and then several times with water. Some isopropanol was added, if necessary, to break any emulsion. Evaporation of the organic phase under vacuum gave 70.9 g of crude sulfonamidoamine I as an oil, free of parent diamine. Potentiometric titration with N/50 HCl showed 91.1% purity. Thus, the actual yield of sulfonamidoamine I was 78%.

When this procedure was performed with a model compound 1-phenylalkane, the crude sulfoamidoamine I was converted to its hydrochloride by dissolving it first in chloroform and then treating the solution with anhydrous hydrogen chloride. Recrystallization of the resulting precipitate from hot isopropanol gave products that, by titration with N/50 sodium hydroxide, gave eq wts that were all within 2% of theoretical values (except for the ethylbenzene derivative, which was within 3%). Each of these hydrochloride salts was converted to the free amine by treatment of its aqueous solution with sodium hydroxide. The liberated amine then was taken up in chloroform. After evaporation of solvent, the neat amine was obtained as a highly viscous oil, which was used as is in the oxidation step that followed.

In a similar manner, sulfonamidoamines $C_nH_{2n+1}C_6H_4SO_2NH(CH_2)_3N(CH_2CH_2OH)_2$ (IV) were prepared from the diamine $H_2N(CH_2)_3N(CH_2CH_2OH)_2$ and alkylbenzenesulfonyl chloride (from 1-phenyloctane and from Nalkylene 500). These amines were not isolable as hydrochloride salts, but titration showed both to be 91% pure.

Amine oxides (III): The procedure of Hoh et al. (4) was used to oxidize the tertiary amines (I) with 30% hydrogen peroxide at 65 C. (Similar oxidation of amines IV led to their corresponding amine oxides V.) A 50% excess of hydrogen peroxide was used for small scale runs (10 g amine). As oxidation proceeded, the reaction mass turned into a highly viscous gel that had to be thinned out by addition of some ethanol to allow proper stirring. Completion of the reaction could be ascertained by dissolving a drop of product in 5 ml water and noting the absence of clouding. Furthermore, the disappearance of tertiary amine (I) was demonstrated by potentiometric titration with N/50 hydrochloric acid; the amine endpoint is seen as a clearly definable inflection point in the pH 5 region, whereas the amine oxide endpoint is a poorly defined one in the pH 3 region. Reactions were essentially quantitative within 15 min at 65 C, when run with 50% excess hydrogen peroxide. Four of the model compound amine oxides (III, n = 6, 8, 10, 12) were cyrstallizable as hydrates from aqueous ethanol.

Picrate salts could be precipitated as oils from a saturated aqueous solution of picric acid upon addition of the amine oxide (III) solution (5). Those picrate salt oils that were further purifiable by crystallization (n = 4, 6, 8, 10, 12) were shown by potentiometric titration with N/100 NaOH to possess eq wts within 2% of the theoretical eq wts of 1:1 amine oxide:picric acid salts. Furthermore, the empirical formulas of one crystalline amine oxide salt (III, n = 6, monohydrate) and its picric acid salt derivative were confirmed by elemental analysis.

Instrumental analyses: Infrared spectra were obtained on a Perkin-Elmer 237 B Spectrophotometer. Amine oxides III were analyzed by differential scanning calorimetry (DSC) on a Perkin-Elmer DSCIB instrument. Nuclear magnetic resonance spectra were obtained on a Jeolco C60H instrument; chemical shifts are reported in ppm downfield from internal tetramethylsilane (δ values). Potentiometric titrations were carried out using a Corning Model 10 pH meter equipped with a Corning rugged combination electrode 476051.

Surface Active Properties

Lime soap dispersing requirements: LSDR were obtained by the Borghetty-Bergman procedure (6).

Detergency evaluations: Screening tests employing a Tergotometer apparatus were carried out as specified in an earlier publication (7). Results are shown in Figure 1 relative to the results obtained using a commercial high phosphate built detergent. Included with performance data for amine oxides III and V are data for Ammonyx TDO, which represented the best performance of the four commercial amine oxides screened.

RESULTS AND DISCUSSION

Preparation of the amine oxide III or that of the sulfobetaine II both involve the common intermediate, amine I, whose yield via the reported pathway (equation 1a) suffered considerable loss (ca. 50%) due to concurrent hydrolysis of the arenesulfonyl chloride. Therefore, the amine synthesis was modified in the present work to take advantage of the tertiary amino group in the diamine to act as scavenger for the HCl by-product (equation 1b). A slight excess of the diamine (10%) was used, and unreacted diamine could be washed out of a chloroform solution of I by aqueous extraction. Further purification of model compounds I then could be achieved via recrystallization of I•HCl. Finally, I was converted to the amine oxide III by a facile reaction with 30% hydrogen peroxide at 65 C. Model compounds III were characterized as their picrate salts.

Proton magnetic resonance spectra aided the identification of intermediates and products. Signal integration was achieved by ratios of signal areas to the areas of the characteristic para substituted benzene ring proton signals. Note the downfield displacements in N-methyl and N-methylene signals (Table I) as the nitrogen achieves more and more positive character ($-CH_2\ddot{N}Me_2$ vs. $-CH_2\overset{+}{N}Me_2—\bar{O}$ vs. $-CH_2\overset{+}{N}Me_2—OH$). The model compound amine oxides III were obtained as crystalline hydrates from cold aqueous alcohol. DSC showed them to undergo changes around 80 C (change of phase), 100 C (dehydration), and 125 C (decomposition). Stability toward decomposition was comparable to that of the commercial product Ammonyx TDO.

In the area of surface active properties, interesting comparisons may be made between the sulfobetaines II and the amine oxides III. The patterns in LSDR (number of g to disperse 100 g sodium oleate in water of 330 ppm hardness) should be noted. Table II shows that the sulfobetaine series of model compounds exhibits a severe drop in LSDR on increasing chain length until an acceptable level of 7 is attained at chain length n = 4. Then a steady improvement continues through n = 10 and 12 (LSDR = 2). On the other hand, the amine oxide series exhibits a severe drop until n = 6 (LSDR = 7), then minimizes at n = 8 (LSDR = 5), and finally the LSDR climbs slightly through n = 12. Note that the LSDR values for the Nalkylene 500-derived compounds II and III are equivalent to those of their n = 12 model compound counterparts. The amine oxides III and V, however, never manifest the efficiency of the sulfobetaine counterparts in LSDR.

Data from detergency screening tests of the series of model compound sulfobetaines II show that detergency increases dramatically from a chain length n = 4 to n = 6, and thereafter slightly through n = 12 (1). Such data from the amine oxide III series, on the other hand, generally show (Fig. 1) achievement of maximum detergency at chain length n = 8 for tallow soap-based formulations (● and ○); at this chain length and in these formulations, performances were similar to or better than the performances of the tallow derived commercial amine oxides. Data are somewhat erratic for the amine oxides by themselves at 0.2% (△), in large part due to great difficulties incurred during rinsing the laundered fabrics; compounds III, n = 8 and 10, adhered strongly to all three fabrics in the absence of soap. There also is a similarity in performances of amine oxides III, n = 8, and V, n = 8 (cf. data for III_8 and V_8 in Fig. 1). The Nalkylene 500-derived amine oxide III (Fig. 1, "III_N") was a disappointing performer. Its branched alkyl group (av n = 11.3) probably is larger than ideal, but detergent alkylates of lower mol wt are not commercially available. None of the amine oxides surpassed the sulfobetaine analogs in detergency performance.

We may conclude, then, that amine oxides III may be synthesized more conveniently than their sulfobetaine analogs II, mainly because of the better safety, cost, and availability of hydrogen peroxide over propanesultone. III also offer the advantage of better solubility; unlike the amine oxides, the sulfobetaines exhibit high Krafft points (8). However, detergency screening tests show III to be surpassed in performance by II.

It is interesting to ponder why the sulfobetaines outperform the amine oxides. LSDA seem to require bulky hydrophilic ends (apparently to prevent inverted soap-LSDA micelles in hard water) (11). There are great differences in charge separation between the two classes of compounds. Recent work has shown that sulfobetaines $R\overset{+}{N}Me_2(CH_2)_x$-$SO_3^-$ and $RCONH(CH_2)_3NMe_2(CH_2)_xSO_3^-$ exhibit better i.e., lower, LSDR as the distance between opposite charges increases from x = 2 to x = 4, but the improvement in LSDR is not dramatic and no similar patterns are seen in detergency screening tests (9). A well performing soap-based formulation generally requires an LSDA that, of its own, is an excellent detergent. The amine oxides are of themselves good detergents, but not comparable to the control (Fig. 1), and are surpassed in performance by their sulfobetaine analogs.

TABLE I

Nuclear Magnetic Resonance Chemical Shift Data for $C_nH_{2n+1}C_6H_4SO_2NH(CH_2)_3N_2Me(I)$ and Related Species

Assignment	Species and conditions			
	I	III	$III \cdot H^+$	$III \cdot H^+$ picrate$^-$
	n=2	n=8	n=8	n=2
	in CCl_4	in acetone-d_6	in acetone-d_6 and CF_3CO_2H	in acetone-d_6 and $CDCl_3$
	at RT[a]	at 46 C	at 46 C	at RT
$N-C-CH_2-C-N$	δ1.63	δ2.2	δ2.4	δ2.3
$-CH_2-Ar$	δ2.73	δ2.78	δ2.82	δ2.81
$-CH_2-N-S$	δ3.05	δ3.07	δ3.25	δ3.16
CH_3-N-C	δ2.18	δ3.25	δ3.75	δ3.76
$-CH_2-N-C$	δ2.25	δ3.48	δ4.08	δ4.06

[a] RT = room temperature.

TABLE II

Lime Soap Dispersant Requirements (LSDR)

Lime soap dispersing agent	LSDR	LSDR of sulfobetaine analog II
Alkaryl amine oxide III		
Alkyl chain length n		
0	150	>100[a]
2	120	80[a]
4	30	7[a]
6	7	4[a]
8	5	3[a]
10	6	2[a]
12	7	2[a]
From Nalkylene 500 detergent alkylate	7	2[a]
Alkaryl amine oxide V		
Alkyl chain length n = 8	6	3[a]
From Nalkylene 500 detergent alkylate	6	2[a]
Commercial amine oxides		
Ammonyx LO	9	4[b]
Ammonyx SO	10	3[c,d] (TSB)[e]
Ammonyx CDO	5	3[b]
Ammonyx TDO	3	3[d] (TASB)[e]

[a] See ref. 1.

[b] See ref. 8.

[c] See ref. 9.

[d] See ref. 10.

[e] TSB = tallow sulfobetaine; TASB = tallow amide sulfobetaine.

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