Preparation of Detergents From Formaldehyde

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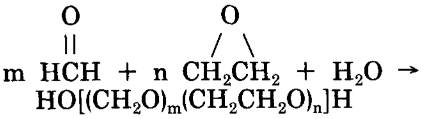
A process was developed for condensing different mol ratios of dodecanol, formaldehyde and ethylene oxide to form a series of adducts with useful detergent properties. These products are analogous to the commercially important class of nonionic surfactants produced by treating fatty alcohols with ethylene oxide to produce a homologous series of adducts. The structures were shown to be represented by $RO[(CH_2O)_x(CH_2CH_2O)_y]R$ where R is either dodecyl or hydrogen, x and y are integers (including zero), and it is understood that the oxymethylene and oxyethylene groups are intermingled in the ether chains. Unfortunately, we were unable to produce commercially viable detergent compositions. For these, our calculations indicate that a dodecanol:HCHO:EO mol ratio between 1:3:4 and 1:5:2 would be necessary both for good detergency and good economics. With acidic catalysts such as BF_3, the condensation is facile and product with desired overall mol ratios can be produced. However, much of the formaldehyde and ethylene oxide are incorporated into by-products that either detract from the detergency properties (e.g., terminal ethers where both R groups are dodecyl) or make the mixtures unacceptable as detergents (e.g., 1,4-dioxane). Because of the presence of terminal ethers, the detergent properties are similar to those of propylene oxide adducts rather than ethylene oxide adducts. With selected basic catalysts most of the harmful by-products can be eliminated, but the reaction rates and conversions are unsatisfactory. Basic catalysts that give high reaction rates convert most of the formaldehyde fed to methyl formate.

Adding traces of formaldehyde to detergent formulations to confer germicidal properties is known. However, no work on actually synthesizing detergents from formaldehyde could be found in the open literature although some earlier work was known to have been carried out within our company (F.B. McAndrew, personal communication).

Polyformaldehyde chains of various lengths form spontaneously, even in aqueous solution, but are hydrolytically and thermally unstable. These chains may be stabilized if both ends are capped by formation of stable groups which block the unzipping reaction. One way of doing this is to polymerize a mixture of formaldehyde and ethylene oxide to form a random copolymer and then deliberately hydrolyze off any formaldehyde end groups to leave a polymer that is end-capped with the more stable 2-hydroxyethyl groups. The preparation of an acetal engineering resin by this route has been practiced commercially for many years (1). The polymerization is illustrated by Chemical Equilibrium 1, where m and n are integers and it is understood that there could be an intermingling of groups derived from formaldehyde and ethylene oxide in the ether chain. The hydrolysis step is represented by Chemical Equilibrium 2, where x and y are integers and it is understood that the groups within the square brackets could be intermingled.



$$m\ \overset{O}{\overset{\|}{HCH}} + n\ \overset{O}{\overset{/\ \backslash}{CH_2CH_2}} + H_2O \rightarrow HO[(CH_2O)_m(CH_2CH_2O)_n]H \qquad [1]$$

$$HO[(CH_2O)_m(CH_2CH_2O)_n]H + n\text{-}y\text{-}2\ H_2O \rightarrow HOCH_2CH_2O[(CH_2O)_x(CH_2CH_2O)_y]CH_2CH_2OH + m\text{-}x\ HCHO + n\text{-}y\text{-}2\ HOCH_2CH_2OH \qquad [2]$$

In practice, only traces of water are present and a high molecular weight polymer containing both oxymethylene and oxyethylene groups in the backbone chain is formed in the reaction represented by Chemical Equilibrium 1.

Our initial goal was to replace the trace of water in Equilibrium 1 with a substantial amount of a fatty alcohol such as 1-dodecanol. A subsequent hydrolysis step, analogous to Equilibrium 2, should produce a stable product. Thus, our hope was to obtain mixtures of formaldehyde-ethylene oxide adducts of dodecanol whose structures could be represented by the following formula where x and y are integers and it is understood that there could be an intermingling of groups derived from formaldehyde and ethylene oxide groups in the ether chain:

$$C_{12}H_{25}O[(CH_2O)_x(CH_2CH_2O)_y]CH_2CH_2OH$$

The product would be a homologous series similar to those formed in the ethoxylation of long-chain alcohols (2). We expected the formaldehyde-containing products to have useful surfactant properties similar to those of ethoxylates because we thought the oxymethylene group should be at least as hydrophilic as the oxyethylene group.

EXPERIMENTAL

Equipment. The reactor was a 300-ml stirred autoclave equipped with an external electrical resistance heater and an internal steam coil. The resistance heater was connected to a temperature indicator controller. The steam coil temperature was set by adjusting the steam pressure. Ethylene oxide was stored under nitrogen pressure in a feed vessel equipped with a calibrated differential pressure cell. The feed vessel and feed line (1/32″ i.d.) were cooled with chilled water (7 to 10°C). The ethylene oxide feed line contained both a manual cut-off and an electrically-operated valve controlled by the reactor pressure.

Safety considerations. Ethylene oxide is only moderately toxic but is a suspected (not proven) carcinogen. It is corrosive, so inhalation and skin contact should be avoided. There are dangerous fire and explosion risks associated with it. Strong acids and bases can catalyze explosive polymerizations in liquid ethylene oxide. Copper, silver or their alloys must be avoided because they are reported to form acetylides that can initiate explosive detonations.

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All equipment containing ethylene oxide was placed behind a barrier in a high pressure cell. The ethylene oxide concentration in the cell and control room was monitored by a photo-detection system sensitive to one ppm. The reactor was equipped with an automatic safety shut-down that would be triggered by either pressure surges or temperature increases above preset levels. The steam coil in the reactor prevents overheating because it can act as a heat sink as well as a heat source. To prevent back-flow from the reactor to the feed line, the ethylene oxide feed vessel was kept under a higher pressure than the reactor, the ethylene oxide was fed into the vapor space of the reactor, and the feed line contained a check valve close to the feed point. All vent lines were run into a scrubber containing a solution of hydrochloric acid and magnesium chloride. A check valve was placed in the line between the reactor and the scrubber, and low pressure nitrogen was fed constantly through this line between the check valve and the scrubber.

During reactions, the nitrogen pressure was adjusted so that the reaction mixtures were always out of the explosive limits.

Condensation procedure. A weighed charge, usually consisting of dodecanol, paraform prills (95+ wt% formaldehyde) and a catalyst was placed into the autoclave. The volume of the charge was selected to provide 150 ml of liquid phase in the reactor when the targeted amount of ethylene oxide was fed. The autoclave was alternately pressured with nitrogen and vented to eliminate air and then heated to reaction temperature. The ethylene oxide was pressured into the autoclave on demand to maintain a pre-determined reactor pressure. When the desired amount of ethylene oxide had been added, the manual valve was closed and the temperature was maintained until essentially complete ethylene oxide consumption was obtained. Normally, this took about 30 min.

Hydrolysis procedure. Samples prepared with BF_3 were filtered through KF. Then, a weighed 50-ml sample of the dodecanol:HCHO:EO adduct was placed into a 150-ml steel bomb and two ml of triethylamine and 25 ml of water were added. The bomb was heated to 190°C for 20 min, cooled, and the contents washed into a tared round-bottomed flask. An additional 50 ml of water was added, and the reaction mixture was distilled at atmospheric pressure until the pot temperature reached 125°C. Yields of recovered product were excellent (greater than 95%). In the worst case (1:1 mol ratio of formaldehyde to ethylene oxide), 0.8% of the formaldehyde charged to the reactor was present in the steam distillate. In the remaining cases (higher ethylene oxide to formaldehyde ratios), less than 0.05% of the formaldehyde fed was recovered as formaldehyde.

The residue was cooled and, if two phases formed, they were separated and weighed. The alcohol:formaldehyde:ethylene oxide ratios were determined by both proton and ^{13}C NMR for both phases. The upper phase contained the majority of material; its alcohol:formaldehyde:ethylene oxide ratios as determined by NMR agreed reasonably well with the ratios charged to the reactor. The lower phases were small and appeared to consist mainly of water, polymers of formaldehyde and ethylene oxide, and ethylene glycol.

TABLE 1

Methane Chemical Ionization Spectra[a]

Series	*m/z*
$I_{1,1}$	135, 117 (11%), 75 (97%), 73 (54%)
$I_{1,2}$	135, 75 (37%), 73 (47%) (no P + 1 detected)
$II_{1,1}$	117, 177 (2%)
$II_{1,2}$	117, 177 (3%) (no P + 1 detected)
III_1	105
III_2	149, 107 (13%), 89 (11%), 87 (16%)
III_3	193, 151 (11%), 133 (12%), 131 (13%), 89 (18%), 87 (18%)
III_4	237, 195 (7%), 193 (1%), 177 (5%), 175 (4%), 149 (4%) 133, (14%), 131 (18%), 107 (2%), 105 (1%), 89 (26%) 87 (21%)
IV_1	147, 105 (11%), 87 (20%)
IV_2	191, 149 (6%), 131 (18%), 87 (19%)
IV_3	235, 193 (8%), 175 (7%), 149 (2%), 131 (25%), 87 (27%)
V_1	73, 133 (16%)

[a] The first peak given is the most intense and the other peak intensities are given as percentages of it. Peaks with *m/z* values less than 73 were not useful in distinguishing among possible structures and are not included. With the exception of III_4 which is used as an example, peaks with intensities less than 5% of the most intense peak are not included unless they are considered significant in interpreting the spectrum.

GC analyses. GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph equipped with a flame ionization detector (FID). The column was a 30-m DB-1 silica capillary column, 0.25 mm i.d., with a one micron film thickness. The carrier gas was helium with a total flow of 90 ml/min. The split ratio was 80:1. The injector and detector temperatures were 350°C. For analyses of the dodecanol:HCHO:EO reaction products, the column was programmed from 100 to 350°C at 10°C/min with a final hold period of 15 min. To separate the light ends or to analyze propanol:HCHO:EO reaction products, the column was held at 50°C for five min and then heated to 350°C at 10°C/min. The hold time at 350°C was 15 min. Peak areas were integrated electronically.

GC sensitivity factors. The GC analyses reported in Table 2 were obtained by normalizing the GC peak areas to 100%. In the calculation of dodecanol:HCHO:EO mol ratios, used in the body of the report, theoretical sensitivity factors (4) were applied to the peak areas of dodecanol adducts.

Determination of Kovat's retention indices. A blend containing all normal paraffins with 5 through 16 carbon atoms and all even-numbered normal paraffins with 18 through 44 carbon atoms was injected into the gas chromatograph using the temperature programs described above. Smooth curves were obtained by plotting peak retention times against carbon numbers. Once retention times for compounds in the reaction products were known, it was possible to read their Kovat's retention indices directly from the appropriate curve. The retention times for the hydrocarbon blend covered the range of the peaks obtained in the analysis.

TABLE 2

GC Analysis of Dodecanol-Formaldehyde-Ethylene Oxide Adducts[a]

Run number		1	2	3	4	5	6	7	8	9
Catalyst[b]		BF_3	TEA	TEA	DABCO	DABCO	BZTM	TEMCL	DABCO	DABCO
Temperature, °C		150	125	50	100	55	122	100	50	50
Conversion[c]		83.9	24.8	47.8	37.1	34.5	8.1	47.5	78.6	21.2
HCHO Source[d]		Prills	Prills	Prills	Prills	Prills	Prills	Prills	Triox	HCHO
Compounds	Structures[e]	Composition of reaction product, wt%								
MeFm		NA	9.0	7.3	4.9	2.7	6.2	4.5		90.1
Dioxolane		NA	1.0		0.6	0.0	0.8	18.8		
Dioxane		NA	1.1		1.6	0.9	2.6	4.9		
Unk[f]		NA	9.0		5.3	0.2	5.7	1.4		
III_1	RE_1	11.1	6.4	1.4	5.7	1.1	6.6	11.0	47.2	0.6
$I_{1,1}$	RM_1E_1	11.7	41.6	36.6	45.1	33.6	41.3	24.9		3.0
III_2	RE_2	2.5	1.3	0.1	3.4	0.2	2.4	1.1	18.1	
$I_{2,1}$	RM_2E_1	2.2	16.2	26.7	15.4	29.9	18.8	11.9		3.3
$I_{1,2}$	RM_1E_2	10.5	1.6	6.9	2.5	0.3	1.4	4.8		
$I_{3,1}$	RM_3E_1		4.9	10.5	4.4	13.6	4.7	4.4		2.0
III_3	RE_3	0.8							16.1	
$I_{2,2}$	RM_2E_2	2.3	2.8	5.4	5.1	3.0	1.2	2.2		
$I_{1,3}$	RM_1E_3	5.6	1.4	3.5	1.5	5.1	2.0	2.1		
$I_{3,2}$	RM_3E_2									1.0
III_4	RE_4	0.8						1.0	10.5	
$I_{2,3}$	RM_2E_3		1.8	2.5	2.7	3.0	0.5	1.8		
$I_{1,4}$	RM_1E_4	3.8	0.4	1.1	0.4	1.7		0.7		
V_1	RMR	22.5							0.8	
$I_{3,3}$	RM_3E_3				0.8	1.7		0.8		
Unknown[g]		2.3	0.4		1.8	0.8	0.4	0.7	5.9	0.7
III_5	RE_5	0.7						1.1	5.2	
V_2	RM_2R	5.0						0.6		
II_1	RMER	9.9				0.5		0.3		
$I_{1,5}$	RM_1E_5	1.2				0.2				
III_6	RE_6							0.3	1.9	
$II_{2,1}$	RM_2E_1R	5.4								
Unknown[g]							0.4	0.1	0.5	0.1
III_7	RE_7								0.7	
III_8	RE_8								0.2	
III_9	RE_9								0.1	

[a] All reactions were run with a dodecanol:formaldehyde:ethylene oxide mol ratio of 1:5:5. Analyses were obtained by normalizing GC peak areas to 100%. They are not corrected for sensitivities.

[b] Catalyst abbreviations are: BF_3, boron trifloride; TEA, triethylamine; BZTM, benzyltrimethylammonium hydroxide; TEMC1, triethylammonium chloride; DABCO, 1,4-diazabicyclo[2.2.2]octane.

[c] Conversions are based on 1-decanol.

[d] Prills are solid polyformaldehyde pellets containing 5 wt% moisture; triox is trioxane, and HCHO is a solution of thermally depolymerized polyformaldehyde in dodecanol.

[e] In the structures for the adducts R represents 1-dodecanol, M represents formaldehyde and E represents ethylene oxide. For example, RM_2E_3 represents the adducts containing one dodecanol, two formaldehyde and three ethylene oxide units.

[f] Unk is a mixture of three unidentified low boiling compounds and 1,3,5-trioxacyclononane.

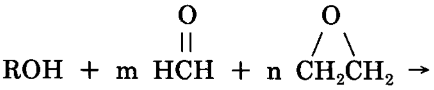
[g] No structure assigned.

GC/MS. A Finnigan series 4000 automated gas chromatograph EI CI mass spectrometer system was used to obtain both electron impact and methane chemical ionization spectra of the reaction products. The m/z values and relative peak intensities for several series of compounds are given in Table 1.

DISCUSSION

The production of ethoxylated alcohols for the detergent trade is a relatively simple operation. The alcohol plus catalyst are heated, and ethylene oxide is added on demand to maintain the desired pressure. Other than perhaps a filtration to remove catalyst, no purification is needed. Any competing process must be equally simple. In addition, an inexpensive source of formaldehyde is needed. Although anhydrous formaldehyde would be better from a chemical standpoint, it would be far too expensive a raw material for a commercial surfactant process. For this preliminary study, we chose to use commercial paraformaldehyde prills that contained 3 to 5 wt% water. Our initial approach was to charge dodecanol, paraformaldehyde prills and a catalyst to a reactor, heat to the desired reaction temperature and then add ethylene oxide on demand to maintain a preset pressure. The hope was that transient intermediates such as the hemiformals of dodecanol and formaldehyde or polyformaldehyde would be ethoxylated as they were formed and thus "captured" as stable materials. (Unlike formals, these hemiformals are not stable compounds. If they could be isolated as pure compounds, they would rapidly re-equilibrate to a mixture of alcohol, formaldehyde, polyformaldehyde and formal at room temperature.)

Acid-catalyzed condensations. With BF_3 as catalyst, the condensation of paraformaldehyde and ethylene oxide with dodecanol is facile. However, the reaction is more complex than envisioned above. As will be shown later, it can best be represented by the Chemical Equilibrium below where most of the structures on the right represent a series of compounds in which the formaldehyde and ethylene oxide units are assumed to be randomly distributed, and R represents the hydrocarbon chain of the alcohol.



$$ROH + m\ \overset{O}{\overset{\|}{HCH}} + n\ \overset{O}{\overset{/\ \backslash}{CH_2CH_2}} \rightarrow$$

$RO[(CH_2O)_x(CH_2CH_2O)_y]H$ ($I_{x,y}$)
+ $RO[(CH_2O)_x(CH_2CH_2O)_y]R$ ($II_{x,y}$)
+ $RO(CH_2CH_2O)_yH$ (III_y)
+ $RO(CH_2CH_2O)_yR$ (IV_y)
+ $RO(CH_2O)_xR$ (V_x)
+ $HOCH_2CH_2O(CH_2O)_xCH_2CH_2OH$ ($VI_{x,y}$)

DETERMINATION OF STRUCTURES

We used a combination of NMR spectra, GC/MS with chemical ionization detection and Kovat's retention indices determined from gas chromatographs to determine the nature of the product.

NMR spectra. The spectra of the products made with dodecanol fit the generalized formula, $C_{12}H_{25}O(CH_2O)_x(CH_2CH_2O)_yH$ where x is the formaldehyde:dodecanol mol ratio and y is the ethylene oxide:dodecanol mol ratio, extremely well. We were able to get useful data on the dodecanol:HCHO:EO mol ratios of the products from both proton and ^{13}C-NMR spectra. In general, they agreed well with the mol ratios calculated from the reaction charges. However, the key point is whether the formula $C_{12}H_{25}O(CH_2O)_x(CH_2CH_2O)_yH$ correctly represents the structure of the majority of the products. As an example, appropriate mixtures of dodecanol:ethylene oxide adducts (III_y) and ethylene oxide:formaldehyde adducts (VI_{xy}) could have an NMR spectra similar to that of $C_{12}H_{25}O(CH_2O)_x(CH_2CH_2O)_yH$. Thus, we were unable to answer this question from NMR spectra alone.

Use of GC/MS and Kovat's retention indices. Initially, the GC/MS was used to obtain electron impact spectra of the reaction products with dodecanol. Examination of these spectra was not helpful because essentially all of the prominent peaks were formed from the hydrocarbon chain of the dodecanol and there were no parent peaks. To aid in identifying the products, several ethylene oxide and formaldehyde:ethylene oxide adducts were prepared using propanol rather than dodecanol as the alcohol. The shorter side chain of the propanol improved the chance of getting usable spectra from the GC/MS. Unfortunately, even this did not produce useful mass spectral scans for the adducts when operating in the normal 70 ev electron impact mode. However, it did permit identification of some of the light ends (e.g., methyl formate, 1,3-dioxolane, 1,4-dioxane; see Table 2.). Finally, the GC/MS was used to obtain chemical ionization spectra with methane as the proton source. The cracking patterns obtained with chemical ionization were simple and informative (Table 1).

The next stage was to apply a variation of Kovat's retention indices that is applicable to temperature programmed gas chromatography (3) to sort the GC peaks into groups of homologous series. When the retention indices assigned to the GC peaks are plotted, the members of a homologous series can be detected by the regular spacing between them. Ultimately, both chemical logic and mass spectra obtained by chemical ionization with methane were used to identify the homologous series. The technique used in assigning structures can be illustrated with Figures 1 through 4. To start, 1-propanol was treated with ethylene oxide using a basic catalyst. Although this reaction is known to give the homologous series represented by structure III_y as the only product, the structures were confirmed by chemical ionization GC/MS (see next page). The GC scan of this product is plotted in Figure 1 with the Kovat's retention indices as the abscissa.

Next, one mol of 1-propanol was allowed to react with five mol of ethylene oxide in the presence of an acidic catalyst (BF_3). The Kovat's retention indices plot is shown in Figure 2. The series III_y are identifiable from Figure 1. The presence of the IV_y series only in the acid-catalyzed reaction is presumptive evidence for terminal ether formation. However, methane chemical ionization spectra were used to confirm the identifications. In the compounds formed from ethylene oxide and 1-propanol alone (see series III_y and IV_y of Table 1), the parent plus one peak was the most intense peak. Ions of the type $ROCH_2CH_2^+$ were prominent (e.g., peaks at m/z 177, 175, 133, 131, 89, 87 in III_4), but those of the type $ROCH_2^+$ were not observed, presumably because their decomposition into HCHO and R^+ is relatively facile. On the other hand, peaks we attribute to ions of the type ROH_2^+ were common (e.g., peaks at m/z 195, 193, 151, 149, 107, 105 in III_4) although usually not as intense as the $ROCH_2CH_2^+$. ions.

Note the regular spacings of both the III_y and IV_y series in Figures 1 and 2. The Kovat's retention indices for the GC peaks are separated by a distance equivalent to 2.5 methylene groups. Because each homologue

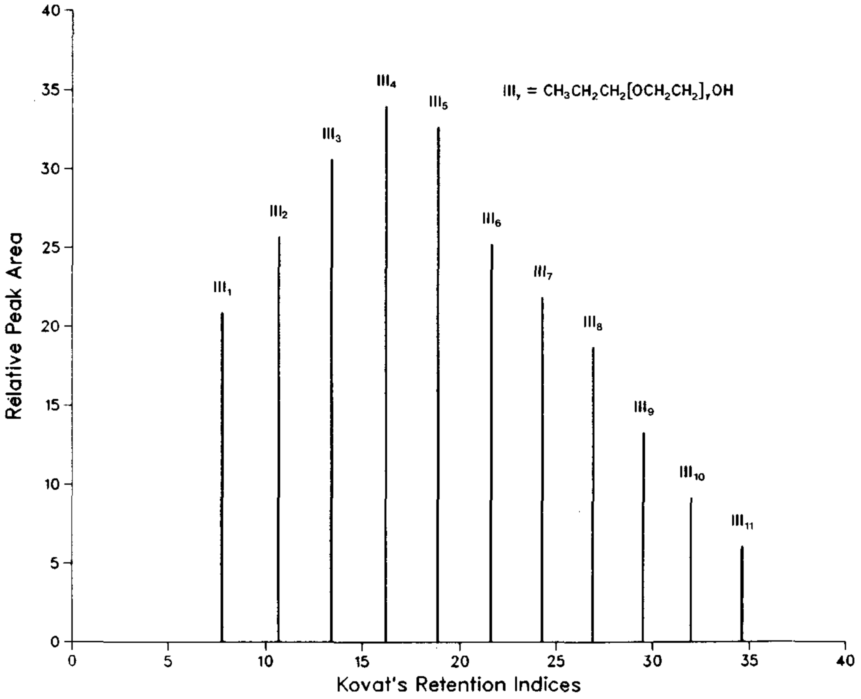


FIG. 1. Kovat's retention indices plot for ethoxylates produced by the reaction of 5 mol of ethylene oxide with one mol of 1-propanol using KOH as the catalyst.

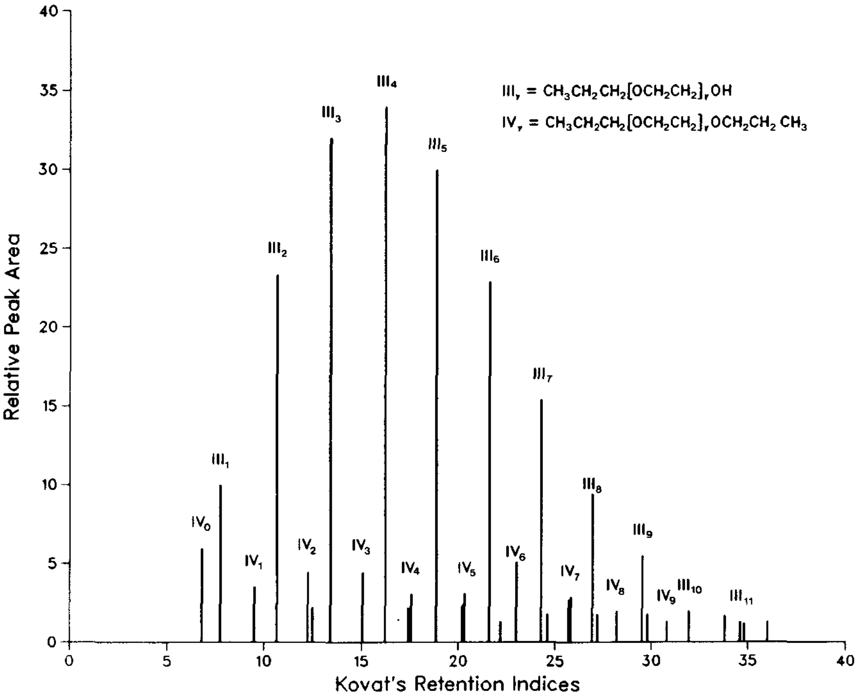


FIG. 2. Kovat's retention indices plot for products produced by the reaction of 5 mol of ethylene oxide with one mol of 1-propanol using BF_3 as the catalyst.

differs from its predecessor by one ethyleneoxy group this implies that the ether oxygen has an effect on retention time equivalent to 0.5 methylene groups. By inference, the methyleneoxy group should have an effect equivalent to 1.5 methylene groups. Later work demonstrated this to be essentially correct.

Figure 3 is a GC scan of the product made by the acid-catalyzed condensation of one mol of 1-propanol, one mol of formaldehyde and five mol of ethylene oxide. Here the peaks with the same retention times as the IV_y series are more intense and a new series, assumed to be II_{xy}, is present. With this sample, use of the GC/MS paid some unexpected dividends. The column used on the GC/MS separated each of the putative

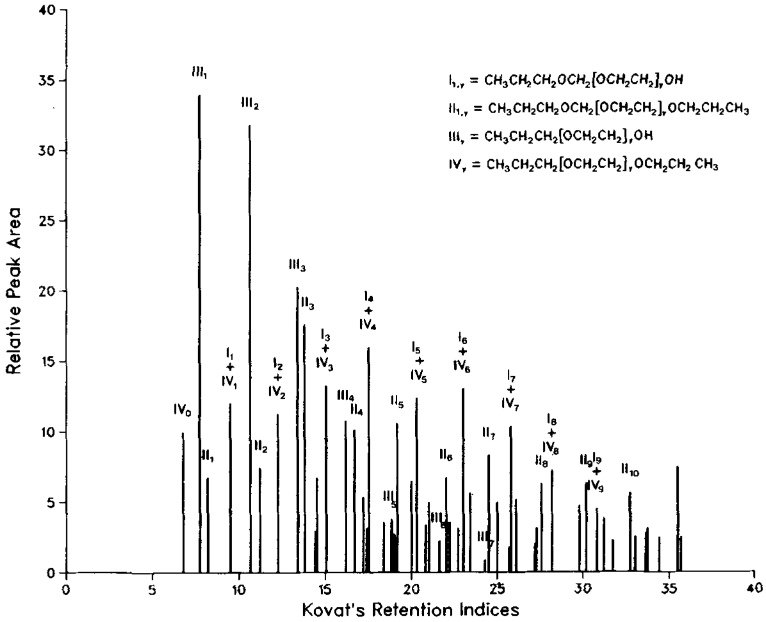


FIG. 3. Kovat's retention indices plot for products produced by the reaction of one mol of formaldehyde and 5 mol of ethylene oxide with one mol of 1-propanol using BF_3 as the catalyst.

IV_y peaks into a doublet. (Our supposedly identical GC column could not make this separation. The differences in performance might have been due to differences in the column exit pressures of the two columns.) The chemical ionization mass spectrum of the front peak of the first doublet showed it to be IV_1. We interpreted (see above) the spectrum of the second (and larger) peak of the doublet to indicate that it was an adduct of one mol each of 1-propanol, formaldehyde and ethylene oxide, i.e., $I_{1,1}$.

By extension, we believe that the series made up of the back peaks of the doublets can be represented as $I_{1,y}$. However, except for $I_{1,1}$, parent peaks could not be detected in the chemical ionization mass spectra to permit an unequivocal characterization. All of the remaining $I_{1,y}$ mass spectra were essentially identical to that of $I_{1,1}$ (Table 1). Our opinion, based initially on the pattern of the Kovat's retention indices, was that the series shown as $II_{1,y}$ in Figure 3 represents the terminal propyl ethers of the $I_{1,y}$ series. This opinion is supported by the absence of the $II_{1,y}$ series from the GC scan (not shown) of the products from base-catalyzed reactions of 1-propanol, formaldehyde and ethylene oxide. Again, except for $II_{1,1}$, parent peaks could not be detected.

In aqueous solution, the acid-catalyzed cleavage of methyleneoxy bonds is many orders of magnitude more rapid than that of ethyleneoxy bonds. Although there are pitfalls in such analogies, there is an obvious similarity between the transition states for these cleavages and the parent plus one ions. (In both, protons are bound to ether oxygen atoms.) Thus, one might expect quantitative differences in the methane chemical ionization spectra of the compounds discussed above (series III_y and IV_y) and those in which one formaldehyde has been incorporated into the chain (Series $I_{1,y}$ and $II_{1,y}$). Thus, with the sole exception of $I_{1,1}$, parent plus one peaks were small or undetectable. The presence of $ROCH_2^+$ ions had to be invoked to explain peaks such as those at m/z 73 and 75 in $I_{1,1}$. Although one would not expect these ions to be stable, one can postulate that because of the presence of methyleneoxy linkages, the parent plus one ions are also quite unstable. Because the spectra represent measurements of the relative stability of the other ions with respect to the parent plus one ion, the relative intensity of the $ROCH_2^+$ ion could be reasonably high.

Mass spectral confirmation for structures in which more than one formaldehyde was incorporated into the ether chain was not obtained. The Kovat's retention indices provide the only evidence for the presence of these compounds.

Because compounds belonging to series $I_{1,y}$ and III_y are unsymmetrical and could fragment from either end, they usually were distinguished by having sets of almost equally intense peaks two mass units apart. To illustrate this, essentially all of the peaks above m/z 87 are listed in Table 1 for III_4.

If our interpretations of the structures of the $I_{1,y}$ and $II_{1,y}$ series are correct, the intensities of their GC peaks should increase when the proportion of formaldehyde in the reaction mixture is increased. Figure 4 shows this to be correct. In addition, GC/MS (using methane chemical ionization) indicates that essentially none of the III_y or IV_y series is present in this sample.

The structures of the dodecanol adducts were worked out using Kovat's retention indices in the same manner as with the propanol adducts, except that no confirmation with GC/MS was available. Even with chemical ionization, useful spectra of the dodecanol adducts were not obtained. In one respect, the work with the 1-dodecanol adducts was simpler; there was no overlap in the GC peaks of the $I_{x,y}$ and IV_y series.

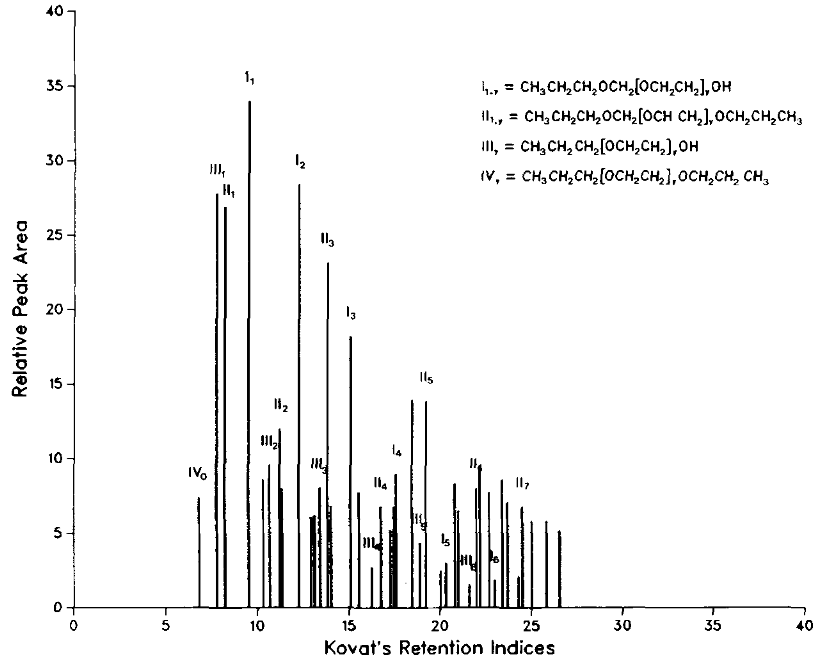


FIG. 4. Kovat's retention indices plot for products produced by the reaction of 5 mol of formaldehyde and 5 mol of ethylene oxide with one mol of 1-propanol using BF_3 as the catalyst.

RESULTS

Most commercial dodecanol-ethylene oxide detergents contain an average of about seven ethylene oxide groups per molecule. Our initial reactions were carried out with the goal of simulating the properties of these detergents with adducts possessing a formaldehyde-ethylene oxide side chain. In these initial runs, the ethylene oxide:dodecanol mol ratios were varied from 5 to 15, and the formaldehyde:alcohol mol ratios from 1 to 10. We believed that this wide variation in mol ratios would help pinpoint the effect of formaldehyde on the properties of the side chain.

The dodecanol:formaldehyde:ethylene oxide ratios of the product, as determined by NMR, agreed reasonably well with the ratios charged to the reactor. In the initial stages of this work, NMR was the only analytical technique available. (It had one obvious shortcoming; it could not be used to determine the nature or distribution of oligomers in the product). At this point, data on critical micelle concentrations (cmc's) and surface tensions above the cmc's were obtained that indicated that the polyether portions of these compounds were more hydrophilic than they would have been if they contained only ethylene oxide. This implied that formaldehyde incorporation into the molecule had taken place. In addition, initial studies on foamability and wetting properties suggested that this class of surfactants showed promise as potential detergents (U.P. Weerasooriya, personal communication).

Shortly afterwards, the development of GC techniques that allowed us to identify the compounds present in the reaction products was completed. The analysis of a product obtained with a 1:5:5 dodecanol: HCHO:EO mol ratio in the feed is shown as run 1 of Table 2. The series of compounds ($I_{x,y}$) incorporating both formaldehyde and ethylene oxide are the main products. In the presence of formaldehyde, only small amounts of the ethylene oxide adducts (III_y) are produced. The key difference between this reaction and the production of acetal resin is the presence of the long-chain alcohol. With acidic catalysts, this alcohol can also act as an end-capping group. Thus, relatively large amounts of the di-dodecyl formal (V_1) and of didodecyl ethers ($II_{x,y}$) are formed. We believe these are undesirable compounds. We think that they are essentially insoluble in water, have poor surfactant properties, and cause the cloudiness observed in aqueous solutions of these materials. We were unable to remove them by extraction because of problems with emulsions. Chemical methods of decomposing them would also decompose the desirable series $I_{x,y}$ compounds.

For run 1, the NMR spectrum indicated that the overall crude product had a dodecanol:HCHO:EO mol ratio close to 1.0:5.0:5.0, in agreement with the mol ratio charged to the reactor. On the other hand, gas chromatography indicated that the volatile portion of the product had a dodecanol:HCHO:EO mol ratio of 1.0:0.67:0.88 (Table 2). The most abundant dodecanol adducts found in the GC scans are those containing only one formaldehyde or ethylene oxide unit. Subsequent GC analyses showed that substantial amounts of formaldehyde and ethylene oxide were converted to low-boiling by-products such as methyl formate, dioxolane and dioxane. However, we believe that about half of the crude product consisted of a polymer of formaldehyde and ethylene glycol (i.e., $VI_{x,y}$ formed via Chemical Equilibrium 1). Formation of this polymer would be initiated by the 3–5% of water present in the paraformaldehyde prills. Although the total amount of water present was small on a weight percent basis, it was large on a mol basis (up to 0.5 mol/mol of dodecanol). A mass balance for run 1 indicates that $VI_{x,y}$ must contain an average of 7 to 9 formaldehyde and ethylene oxide units. We believe that most of this material does not show up on gas chromatograms, presumably because of its polarity and high molecular weight.

If one assumes that one methyleneoxy group is equivalent to one to one and one-half ethyleneoxy groups in conferring water solubility, then to mimic the detergency properties of oligomers of dodecanol and ethylene oxide having an average mol ratio of 1:7 it would be necessary to have a dodecanol:HCHO:EO mol ratio between 1:5:2 and 1:3:4. These high formaldehyde mol ratios would also be needed to make a product that is less expensive than the dodecanol-ethylene oxide adduct. In addition, for a commercially viable process, essentially all of the formaldehyde and ethylene oxide fed to reactor must be converted to desirable products. While it would be desirable to use anhydrous formaldehyde rather than commercial paraformaldehyde, the high cost of the anhydrous material prohibits its use for preparation of a commercial detergent. Thus, synthetic work was concentrated on finding catalysts and reaction conditions that could eliminate the formation of low-boiling impurities, reduce the amount of end group etherification, and essentially eliminate the formation of the formaldehyde-ethylene oxide polymer, $VI_{x,y}$.

Both lower reaction temperatures and milder Lewis acid catalysts were tested as approaches for attaining these goals. These approaches were not successful. At lower reaction temperatures with BF_3 as catalyst, $VI_{x,y}$ makes up a much larger proportion of the product. On the other hand, the milder acidic catalysts such as $SnCl_4$, $SbCl_5$, and $Ti(OCH_3)_4$ appear to require high reaction temperatures. We got either no reaction or exothermic, difficult to control reactions with these catalysts.

Basic catalysts. Because the etherification reaction is inherent in acid catalysis, we broadened our search to include basic catalysts. Our initial work demonstrated that the standard basic catalysts used for ethoxylations [e.g., barium phenolate, potassium hydroxide, $Ca_3(PO_4)_2$] were ineffective in the presence of formaldehyde. Presumably, they catalyze a Cannizarro reaction to produce methanol and formic acid. The formic acid then neutralizes the catalyst.

Triethylamine was the first basic catalyst with which the dodecanol:HCHO:EO condensation worked, but it was not a satisfactory catalyst. Although it was possible to initiate reactions, they were not sustained and conversions were low. When about one-tenth of the desired amount of ethylene oxide had been added, a pressure surge (>100 psig) triggered the safety shutdown system. At first, this pressure surge was puzzling. There was always an induction period. There was no measurable temperature change. Vent samples taken after the surge contained about 8% carbon monoxide but no detectable hydrogen. If the excess pressure was vented, the reactions could not be restarted by adding more ethylene oxide. Our interpretation of these data is that a Cannizarro-type reaction occurred which converted formaldehyde into methanol and formic acid. We posit that the triethylamine reacted with ethylene oxide to form a betaine that could catalyze the rapid decomposition of the formic acid (or its salt) to carbon monoxide and water. As required by this concept, methanol was present in the liquid phase of the reaction product.

To facilitate comparison of acidic and basic catalysis, a series of runs was carried out with dodecanol:HCHO:EO ratio of 1:5:5 in the feed (Table 2). The volatile product from the initial run with triethylamine as catalyst (run 2 of Table 2) had a dodecanol:HCHO:EO mol ratio of 1.0:1.28:1.15 based on GC analysis. The amount of low-boiling by-products was considerably less than with acidic catalysts. However, the dodecanol conversion was only about 25% compared to about 85% for acid catalyzed runs. The lower dodecanol conversion implies that more of the formaldehyde-ethylene oxide polymer, $VI_{x,y}$, is produced. Thus, overall results are still unsatisfactory. Lowering the reaction temperature to 50°C (run 3 of Table 2) improved the dodecanol conversion to about 50%, but the mol ratio in the dodecanol adducts was still only 1.0:1.55:1.27.

In an effort to improve the yields, a number of other catalysts were tested. These included 1,4-diazabicyclo[2.2.2.]octane (DABCO) (runs 4 and 5) and benzyltrimethylammonium hydroxide (run 6). No carbon monoxide formation was observed with these catalysts. However, in other aspects the catalysts were not appreciably better than triethylamine.

Next, we attempted to get higher dodecanol conversions by optimizing the reaction temperatures and pressures. The most effective catalyst was DABCO. A number of runs was made at lower temperatures (60°C and below). In the best of these, (run 5 of Table 2) the volatile product had a dodecanol:HCHO:EO mol ratio of 1.0:1.67:1.28 based on GC analyses. In addition, very low levels of methyl formate and 1,4-dioxane were present. However, the dodecanol conversions were only about 35% so the reaction efficiencies were far short of those needed. The NMR spectrum again indicated that the overall product from basic catalysis had a "true" dodecanol:HCHO:EO mol ratio close to 1:5:5. Thus, a mass balance indicates that about 80% of the product must consist of the formaldehyde-ethylene oxide adducts, $VI_{x,y}$.

The low conversions with basic catalysts appear to be mainly a kinetic rather than a thermodynamic problem. Catalysts are needed that catalyze the reaction of dodecanol rather than water and give the right balance of rates with formaldehyde and ethylene oxide. In addition to benzyltrimethylammonium hydroxide, triethylamine and DABCO, we tested some essentially neutral or slightly acidic catalysts. These included tetraethylammonium chloride, tributylphosphine, triphenylphosphonium phenolate, triphenylphosphonium iodide, tetramethylammonium chloride, tetrabutylphophonium bromide, methyl iodide, molecular iodine, N-methyl-2-pyrrolidinone, tris(butoxymethyl) amine, hexamethylenetetramine, carbon and Bi_2O_3. All of these are reported to catalyze the polymerization of anhydrous formaldehyde effectively. As catalysts, tetraethylammonium chloride, tetramethylammonium chloride, and the triphenylphosphonium salts gave results similar to those with DABCO but appear to be slightly acidic. The best results were obtained with tetraethylammonium chloride (run 7 of Table 2). More light ends (including dioxolane) plus traces of didodecyl formal were produced. The conversions were not significantly higher than with DABCO. The other catalysts listed above were less effective. The main products with most of them were light ends. With N-methyl-2-pyrrolidinone, methyl formate and dioxane were the sole products.

With DABCO as catalyst, no formaldehyde was incorporated into the product when the paraformaldehyde in the feed was replaced with trioxane (run 8). This means that internal ether linkages cannot be cleaved with these basic catalysts. We take this to indicate that only the formaldehyde unit at the end of the paraformaldehyde chain is available for reaction when basic catalysts are used. Trioxane reacted readily when BF_3 was used as catalyst.

Condensations with molecular formaldehyde. Several attempts were made to break the paraformaldehyde down into formaldehyde, form an adduct with dodecanol, and react the adduct with ethylene oxide. In the first set of runs, a mixture of dodecanol and paraform prills was heated to 160°C for an hr to depolymerize the paraformaldehyde. The temperature was then lowered to 50°C, and an attempt was made to add ethylene oxide. With DABCO, DABCO plus copper acetylacetonate, calcium acetylacetonate, or triethylamine as catalysts, no reaction could be initiated.

Next, paraform was thermally decomposed and the resulting gaseous formaldehyde was absorbed in dodecanol. As quickly as possible, this solution was placed in a reactor and addition of ethylene oxide was started. Reaction could be initiated with DABCO as catalyst. Typical results are shown in run 9. The only adducts detected were the desired ones containing both formaldehyde and ethylene oxide. However, methyl formate was by far the major product in these runs.

COMMERCIAL UTILITY

Although we have been able to prepare condensation products of dodecanol, paraformaldehyde and ethylene oxide that have surfactant properties, we have not found catalysts and reaction conditions that produce a commercially viable detergent. For this, our studies indicate that a dodecanol:HCHO:EO ratio between 1:3:4 and 1:5:2 is needed. The high formaldehyde content is necessary for good economics (i.e., prices below those of the corresponding ethylene oxide adducts) as well as good detergency. With acidic catalysts such as BF_3, the condensation of dodecanol, paraformaldehyde prills, and ethylene oxide is facile. Products with detergency properties similar to those of propylene oxide adducts but not as good as those of ethylene oxide adducts were obtained. In our opinion, the detergency properties would have been much improved if formals and the terminal ethers with dodecanol could have been eliminated. However, it would still have been necessary to drastically reduce the formation of formaldehyde-ethylene oxide polymer and to eliminate the formation of traces of dioxane. Dioxane is an insidious product because it is a suspected carcinogen. This alone would prevent the use of these adducts as detergents. In any case, the formals and terminal ethers are formed in such high concentrations that they drastically reduce the surfactant properties of the mixtures. Anhydrous formaldehyde is so costly that its use to eliminate formation of the formaldehyde-ethylene oxide polymers was not an option.

The use of basic catalysts did allow us to eliminate some of the undesirable side products (terminal ethers and formals) produced with acidic catalysts. However, basic catalysts did not completely eliminate 1,4-dioxane as a trace by-product (Table 2). Moreover, the dodecanol conversions are only 50% or less and about 10% of the formaldehyde that reacts is diverted to methyl formate. The dodecanol conversions are low because only the terminal formaldehyde group is cleaved from the paraformaldehyde and made available for reaction when basic catalysts are used. In contrast, acidic catalysts can cleave any of the ether linkages in paraformaldehyde (or trioxane), and the overall reaction is rapid.

By absorbing gaseous formaldehyde in dodecanol, a solution can be prepared that contains relatively low molecular weight formaldehyde species. Attempts to use basic catalysis to produce dodecanol:HCHO:EO adducts from such solutions have been futile. Because of the high free formaldehyde content the Cannizarro reaction predominates and at least 90% of the formaldehyde is converted to methyl formate.

Thus, with basic catalysis we have a dilemma. The Cannizarro reaction can be suppressed by using paraformaldehyde as a formaldehyde source because this keeps the free formaldehyde concentration low. However, this leads to low reaction rates and the ultimate result is an unacceptably low conversion to products containing dodecanol. Increasing the free formaldehyde concentration favors the production of methyl formate and essentially eliminates the desirable condensation reactions. We see no simple way out of this dilemma.

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