A Comparison of the Ethoxylation of a Fatty Alcohol, Fatty Acid, and Dimethiconol

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ABSTRACT: Knowing that dimethiconols or silanols condense under acid or alkaline catalysis, a study was undertaken to determine if these compounds could be successfully ethoxylated under conditions similar to those used to ethoxylate fatty alcohols and acids. It was anticipated that the condensation reaction would take precedent over ethoxylation reaction. We determined that ethoxylation reaction occurs preferentially to condensation reaction. In addition, kinetics of ethoxylation are similar to kinetics observed when fatty alcohols are ethoxylated. This reaction gives rise to a new class of hydrolyzable silicone compounds that have applications in industrial as well as in personal-care products.

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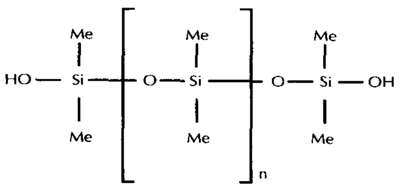
KEY WORDS: Alkoxylation, dimethiconol, ethoxylation, ethylene oxide, fatty acid, fatty alcohol, polysiloxanes, silanol, silicone.

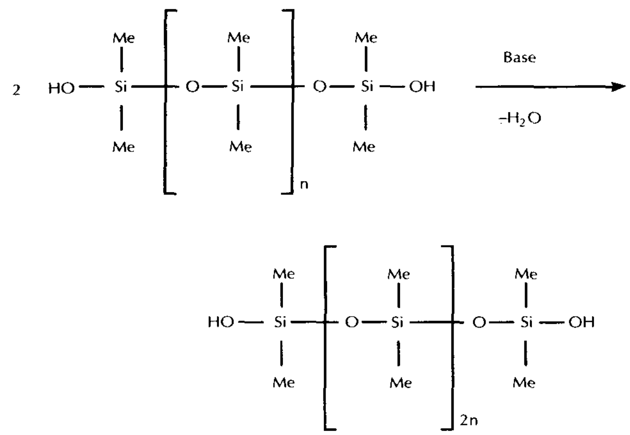
Dimethiconol compounds, also referred to as silanol compounds, unlike silicone fluids, have a reactive hydroxyl group on the terminal portion of the molecule. Unlike fatty alcohols, the hydroxyl group is bonded directly to the silicon atom in an Si-OH bond rather than a CH_2-OH bond. The structure is as follows:



$$HO-Si(Me)_2-[O-Si(Me)_2]_n-O-Si(Me)_2-OH$$

When dimethiconols undergo condensation reactions in the presence of acid or base, there is an increase in molecular weight (an increase in the *n* value), and water is produced. This is why silanol compounds may develop a haze and gel upon standing. Reactivity of the terminal silanol (Si-OH) group makes these compounds useful in the preparation of room temperature–vulcanizable silicone sealants (1).

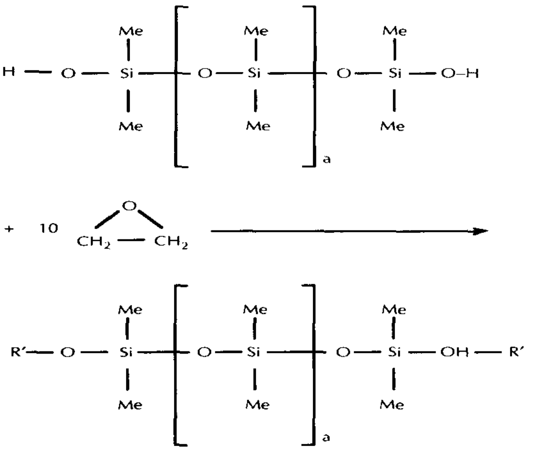
Dimethiconol condensation reaction sequence. The condensation reaction results in high-molecular weight polymers is expected when compounds containing silanol groups are exposed to acid or base catalysis:



$$2\ HO-Si(Me)_2-[O-Si(Me)_2]_n-O-Si(Me)_2-OH \xrightarrow[-H_2O]{Base} HO-Si(Me)_2-[O-Si(Me)_2]_{2n}-O-Si(Me)_2-OH$$

However, because silicon and carbon atoms share many similar properties and occur in the same column in the periodic table, we expected that the Si-OH hydroxyl could also be ethoxylated like the C-OH group. We expected this reaction to be competitive with the condensation reaction. If the ethoxylation reaction did in fact compete, we desired to determine to what extent the reactions competed, as well as the kinetics of the reaction.

Dimethiconol ethoxylation reaction sequence. When 10 moles of ethylene oxide (EO) are reacted with one dimethiconol molecule, the average R′ becomes $-(CH_2-CH_2-O)_5-H$:



$$H-O-Si(Me)_2-[O-Si(Me)_2]_a-O-Si(Me)_2-O-H + 10\ CH_2-CH_2(O) \longrightarrow R'-O-Si(Me)_2-[O-Si(Me)_2]_a-O-Si(Me)_2-OH-R'$$

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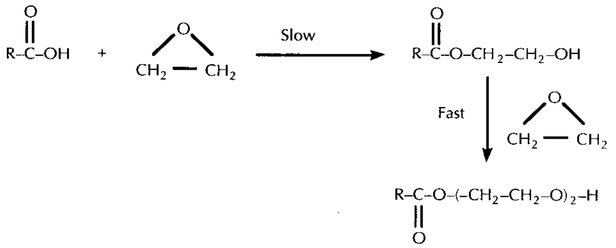
The exact value of the number of moles of EO condensed onto each silanol will be a distribution of values averaging 5.

An induction period is expected in the ethoxylation of fatty acids and is a consequence of the fact that the reaction of the first mole of EO is slower than the subsequent ethoxylation of the resulting hydroxyl group:



We therefore realized that the presence of an induction period in the ethoxylation of dimethiconol would show that the Si-OH group was less reactive than the C-OH group formed upon addition of the first mole of EO. Therefore, simply stated, if the silanol group could be ethoxylated, it would either (i) ethoxylate with an induction period, like a fatty acid, or (ii) lack an induction period, like a fatty alcohol.

If an induction period was noted, the following could be stated about the reaction kinetics:

$$\text{Si-OH} \xrightarrow{\text{Slow}} \text{Si-O-CH}_2\text{CH}_2\text{-OH} \xrightarrow{\text{Fast}} \text{Si-(-O-CH}_2\text{CH}_2)_2\text{-OH}$$

If no induction period were noted, the following would be the situation:

$$\text{Si-OH} \xrightarrow{\text{Fast}} \text{Si-O-CH}_2\text{CH}_2\text{-OH} \xrightarrow{\text{Slow}} \text{Si-(-O-CH}_2\text{CH}_2)_2\text{-OH}$$

or

$$\text{Si-OH} \xrightarrow{\text{Fast}} \text{Si-O-CH}_2\text{CH}_2\text{-OH} \xrightarrow{\text{Fast}} \text{Si-(-O-CH}_2\text{CH}_2)_2\text{-OH}$$

Based on the similarity of Si and C atoms, we expected the latter to be observed.

Ethoxylation of fatty compounds. Because our comparison was to fatty compounds, the following is pertinent about the ethoxylation of fatty alcohols and acids: EO reacts in an extremely exothermic manner with compounds having a labile hydrogen. Fatty acids and fatty alcohols are two of many classes that contain a labile hydrogen. Alkaline and acidic catalysts make the reaction possible and accelerate it.

Fatty alcohol ethoxylation. Fatty alcohols react with EO at the hydroxyl group to give an ether linkage and a new hydroxyl group. Although the reaction is conceptually simple, the reality is that the reaction product is a complex mixture of oligomeric products that are a series of compounds with different amounts of EO (2). There is relatively wide distribution of species that have varying amounts of EO on the base hydrophobe.

TABLE 1
Ethoxylation of Stearyl Alcohol with One Mole Ethylene Oxide (EO)[a]

Designation	Moles of EO (value A)	Area % (value B)	EO contribution (values A and B)
18-0	0	60.3	0.000
18-1	1	13.6	0.136
18-2	2	8.8	0.176
18-3	3	7.9	0.237
18-4	4	5.9	0.236
18-5	5	2.2	0.110
18-6	6	0.9	0.054
18-7	7	0.3	0.021
18-8	8	0.1	0.008

[a] Total calculated moles added was 0.978.

Our analysis of the products that are produced when one mole of EO is reacted with one mole stearyl alcohol is shown in Table 1. The analysis was done *via* gas–liquid chromatography.

Table 1 shows that when one mole of EO is reacted with one mole of fatty alcohol, adducts with no added EO predominate in the mixture and comprise 60.3% of the mixture. The other adducts, ranging from 1–8 moles of EO, comprise the remainder. If the amount of EO found on each adduct is multiplied by the percentage of that adduct, EO contribution is calculated. The difference between the observed 0.978 moles and the 1.0 added moles is primarily due to polyoxyalkylene glycol formation (3).

Fatty acid ethoxylation. Fatty acids, when reacted with EO, produce complex mixtures of hydroxy esters. Unlike the products formed by the ethoxylation of fatty alcohols, which are ethers, esters are formed when EO is reacted with fatty acids. In addition to the oligomeric species that form during the reaction of a fatty acid with EO, there is an added complication. That complication is the formation of a diester:

Monoester	Diester
$\text{R-C(O)-O-CH}_2\text{CH}_2\text{OH}$	$\text{R-C(O)-O-CH}_2\text{CH}_2\text{OC(O)-R}$

Table 2 shows published data on the ratios of mono- to-diesters (4).

As stated earlier, the salient difference between fatty acid ethoxylation and fatty alcohol ethoxylation under alkaline catalysis is that the former has an induction period. During this early stage of reaction, there is a period of time where negligible amounts of product are formed. After initial induction period, reaction rate increases to about that of the fatty alcohol.

Ethoxylation of fatty acids, like that of fatty alcohols, will not occur without catalyst. The catalyst can be either acidic or more typically alkaline. Alkaline catalysts generally produce less by-products.

TABLE 2
Ethoxylation of Fatty Acids

Hydrophobe	Moles EO	Monoester	Diester	PEG[a]
Stearic acid	9.0	38.9	41.1	20.0
Oleic acid	13.6	59.7	26.8	13.5

[a] PEG, Polyoxyethylene glycol; other abbreviation as in Table 1.

Dimethiconol ethoxylation. As shown previously, ethoxylation of the silanol bond would result in formation of a Si-O-C bond, which is hydrolyzable. The Si-C bond, however, is nonhydrolyzable. This situation is analogous to sulfate and sulfonate compounds in fatty chemistry. The hydrolyzable products are retroreactions that give the starting silanol and polyoxyethylene glycol (PEG) in the case of the silanol ethoxylate, or fatty alcohol, and inorganic sulfate in the case of the fatty alcohol sulfate.

EXPERIMENTAL PROCEDURES

Siltech S-701 (Siltech, Norcross, GA), a silanol with a molecular weight of 4211, was ethoxylated under the following conditions: (i) The specified amount of the silanol was added to a clean, dry ethoxylation vessel that can be heated to 200°C and can accommodate pressures of up to 100 psig; (ii) 0.1% KOH (95%) was added under good agitation; (iii) The reaction mixture was heated to 270°F and stripped under vacuum for 1 h; (iv) EO was added at 270°F and 45 psig; (v) The amount of EO added as a function of time and was recorded at constant pressure and temperature; and (vi) After all the EO was added, the reaction mixture was held at temperature for 1 h.

RESULTS AND DISCUSSION

The following results were obtained: (i) Table 3 shows the amount of EO added to various hydrophobes with 0.1% KOH catalyst. Stearyl alcohol adds 4.2 moles EO in 2 h, dimethiconol has 5.0 moles added in the same period, while stearic acid has only 0.8 moles added. Schick (5) previously evaluated ethoxylation of stearic acid and stearyl alcohol in his now-classic work. While his conditions were different, results are comparable to those of the current work; (ii) No condensation was observed during the reaction under the conditions studied. This was confirmed by gel permeation chromatography; (iii) A white waxy product was produced during the process; (iv) There was no induction period encountered. In fact, in the early part of the reaction sequence, dimethiconol ethoxylated slightly more rapidly than fatty alcohol and much more rapidly than fatty acid; (v) Resulting product from ethoxylation is a surface-active agent that goes from water-insoluble to water-dispersible to water-soluble. In short, the silicone hydrophobe acts like a fatty hydrophobe as EO is added.

TABLE 3
Moles of Ethylene Oxide Added vs. Time at Reaction Conditions[a]

Time (h)	Nonylphenol	Stearyl alcohol	Siltech S-701[b]	Stearic acid
0.0	0.0	0.0	0.0	0.0
1.0	4.9	1.1	1.5	0.5
1.5	7.5	2.5	3.0	0.6
2.0	9.5	4.2	5.0	0.8
2.5	11.1	7.0	7.8	3.0

[a] 270°F, 45 psig, 0.1% KOH.
[b] Siltech, Inc. (Norcross, GA).

TABLE 4
Properties of Surface-Active Agents as Functions of HLB[a]

Solubility in water	HLB value	Description
Insoluble	4–5	Water-in-oil
Poorly dispersible (milky appearance)	6–9	Wetting agent
Translucent to clear	10–12	Detergent
Very soluble	13–18	Oil-in-water

[a] HLB, Hydrophile–lipophile balance.

Hydrophile–lipophile balance (HLB) considerations. We attempted to apply the HLB concept to products from the above reaction. We used the following formula:

$$\%EO/5 = HLB$$

This works for fatty alcohol ethoxylates but is of limited application for many other surface-active agents. HLB is the ratio of oil-soluble and water-soluble portions of a molecule. The system was originally developed for ethoxylated products. Listed in Table 4 are some approximations for HLB values of surfactants as a function of their solubility in water (6).

Listed in Table 5 is the observed water solubility for the silanol ethoxylates. As can be seen, silanol materials are somewhat less water-soluble than would be expected from application of the HLB formula.

Maximum ethylene oxide added. Ethoxylation of ethylene glycol to produce polyoxy EO is carried out commercially by many manufacturers. There is a practical limitation of as to how high a molecular weight can be attained with KOH as a catalyst (7). The practical molecular weight to which ethoxylation can be carried is 8,000. This product is commonly called PEG 8,000. If one continues to ethoxylate beyond this molecular weight, degradation of the polymer occurs, which leads to terminal unsaturation and lower molecular species. To see if this also occurs during ethoxylation of silanols, we continued to ethoxylate the silanol to determine at what point the reaction rates fell to negligible, and then we compared the number of moles added to that of ethoxylating ethylene glycol.

Table 6 indicates that the maximum number of moles of EO that can be added is comparable for the ethylene glycol and the silanol products.

In conclusion we can state that dimethiconol compounds can be ethoxylated with 0.1% KOH as a catalyst (8). The ex-

TABLE 5
Water Solubilities of Three Different Silanol Ethoxylates[a]

Product	%EO	Theoretical HLB	Theoretical water solubility	Observed water solubility
1	50	10	Dispersible	Poorly dispersible
2	60	12	Soluble	Dispersible
3	70	15	Soluble	Soluble

[a] Abbreviations as in Tables 1 and 4.

TABLE 6
Comparison of Maximum Level of EO Addition to Ethylene Glycol and Silanol[a]

Material	Maximum moles EO	PEG
Ethylene glycol	181	8,000
Silanol	176	7,744

[a]Abbreviations as in Tables 1 and 2.

pected condensation reaction does not occur under those conditions. We can also state that the product ethoxylation of dimethiconol is a hydrolyzable silicone compound. In addition, there is no induction period observed when ethoxylation is carried out. This implies that the reaction of the silanol hydroxyl group with EO is not the rate-limiting step. The first mole of EO adds to the dimethiconol at a rate equal to or faster than the rate at which EO adds to the resulting CH_2-OH group.

Also, when HLB of the resulting dimethiconol ethoxylate is calculated by the standard formula, observed water solubility varies only slightly from the predicted value. Dimethiconol ethoxylate is slightly more hydrophobic than predicted.

Finally, the amount of EO that can be added to dimethiconol before reactivity is lost is approximately equal to the amount that can be added to ethylene glycol in producing high-molecular weight PEG.

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