Monoethoxylation of Hindered Carboxylic Acids[1]

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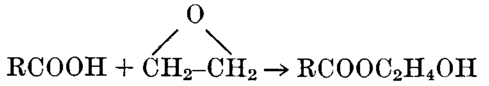
Abstract

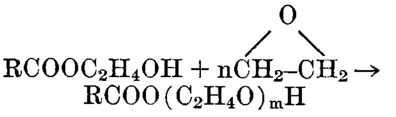
Polyethoxylates of unhindered fatty acids are well known as surface active agents. The monoethoxylates of these acids, however, are difficult to prepare in good yields. It has now been demonstrated that monoethoxylates of hindered aliphatic acids can be prepared in high selectivity and conversion. Experimental conditions are reported which overcome serious side reactions prevalent with unhindered acids.

Introduction

The reaction of ethylene oxide with fatty acids to yield polyethylene glycol monoesters is well known. These polyethoxylates find wide-spread use as surface active agents. On the other hand, monoethoxylates of fatty acids are not generally available. Their preparation in good yield is difficult because of competing side reactions that produce significant amounts of byproducts (1). The reaction is customarily conducted with an alkaline catalyst and in addition to the monoethoxylate [1], polyethoxylates are produced by the further reaction of the monoethoxylate with ethylene oxide. Likewise, diesters of ethylene glycol and polyethylene glycols can be formed by ester exchange and by direct esterification of the ethoxylates [2–4] (2,3).



$$RCOOH + \overset{O}{CH_2{-}CH_2} \rightarrow RCOOC_2H_4OH \quad [1]$$



$$RCOOC_2H_4OH + n\overset{O}{CH_2{-}CH_2} \rightarrow RCOO(C_2H_4O)_mH \quad [2]$$

$$2RCOO(C_2H_4O)_mH \rightarrow RCOO(C_2H_4O)_mOCR + HO(C_2H_4O)_mH \quad [3]$$

$$RCOOH + RCOO(C_2H_4O)_mH \rightarrow RCOO(C_2H_4O)_mOCR + H_2O \quad [4]$$

$(m = n + 1)$

Considerable control over the formation of polyethoxylates can be exercised by limiting the amount of ethylene oxide relative to carboxylic acid employed in the ethoxylation. But the formation of diesters is difficult to control. The ethoxylation of fatty acids such as lauric and stearic acids has previously been reported to give appreciable yields of ethylene glycol diesters (4). In a study of the ethoxylation of hindered carboxylic acids we discovered that if the ester group of the monoethoxylate were sufficiently hindered, almost quantitative control of ester exchange and esterification leading to diester formation was possible.

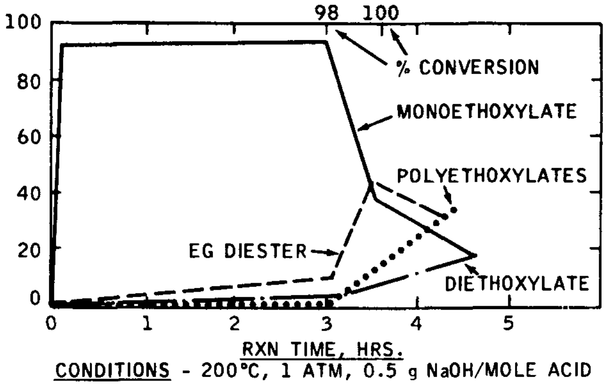


FIG. 1. Ethoxylation of neo-decanoic acid effect of conversion on product selectivity.

Experimental Procedures

Starting Materials

As hindered acids for our study we initially chose the neo-acids which are commercially available from Enjay Chemical Company. Most of our studies were on the C_{10} neo-acid, neo-decanoic acid, but the results were also readily extended to neo-pentanoic acid (pivalic acid). The alpha carbon atom configuration of neo-decanoic acid is 67% α,α-dimethyl, 31% 2-methyl-2-higher-alkyl and 2% di-higher, alkyl, where the alkyl group can be ethyl or higher homologs. Neopentanoic acid is exclusively trimethyl-acetic acid. Commercial ethylene oxide, sodium hydroxide, n-decanoic acid, 2-ethylhexanoic acid and isobutyric acid were used without further purification.

Methods

Our studies consisted primarily of laboratory ethoxylations at atmospheric pressure. A 1-liter, four-necked flask fitted with a water-cooled stirrer, condenser, thermometer and gas dispersion thimble was connected through two 500 ml safety bottles to a graduate containing Primol 185 and a manifold. The manifold was, in turn, connected to a source of low pressure nitrogen and to a tank of ethylene oxide. Neo-decanoic acid was charged to the flask, followed by powdered sodium hydroxide as a catalyst. A slow stream of nitrogen was started through the acid and the temperature was raised to 150 C (during this time the water formed by reaction of the sodium hydroxide with the neo-decanoic acid was driven off). Ethylene oxide gas was admitted to the manifold and allowed to escape momentarily to the atmosphere through a three-way stopcock. The stopcock was then turned to vent nitrogen to the atmosphere and ethylene oxide was simultaneously introduced into the flask.

Absorption took place slowly with no rise in temperature. The ethylene oxide rate was increased to the point where an occasional bubble of oxide escaped through the Primol. The temperature was maintained at 150 C until a conversion of about 98% was obtained, as measured by titration of residual acid (phenolphthalein end point). To determine product selectivity, samples were periodically removed with a syringe and analyzed by gas chromatography. In shutting down, the ethylene oxide feed was vented to the air, and nitrogen was turned into the flask. A slow stream of nitrogen was maintained until all of the ethylene oxide had been purged from the system.

After cooling to room temperature, neo-decanoic acid monoethoxylate was isolated in 95% yield by washing successively with 5% sodium hydroxide and then with water until neutral. This was followed by short path vacuum distillation. The product distilled at 126–129 C/3.2 mm Hg.

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TABLE I
Ethoxylation of Neo-Decanoic Acid vs *n*-Decanoic Acid[a]

Acid	Time hr	Per cent conv.	Per cent selectivity		
			Mono-ethoxylate	EG diester	Higher ethoxylates
Neo-Decanoic	3	98	92	6	2
n-Decanoic	3	96	9	86	6

[a] Conditions: 200 C, 1 Atm, 0.5 g NaOH/mole acid.

Product Analysis

Product composition was determined by gas chromatography using an F&M 720 instrument equipped with a 3 ft column of 10% silicon gum rubber on chromosorb W. A 60 cc/min gas flow rate was used and a 5.6 C/min program starting at 100 C and holding at 340 C. Neo-decanoic acid monoethoxylate eluted at 145 C.

Identification of neo-decanoic monoethoxylate and ethylene glycol di-neo-decanoate was accomplished by both elemental analysis of the fractionally distilled product and by Time of Flight mass spectrometry. The absence ($<0.1\%$) of polyethylene glycol in the still bottoms was determined by infrared analysis and by liquid distribution between ethyl acetate and aqueous sodium chloride solution (5).

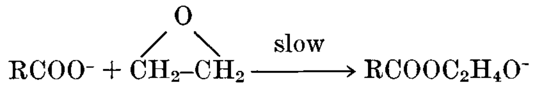
Results and Discussion

Table I shows that ethoxylation of neo-decanoic acid gives selectivity (composition of ester) to monoethoxylate of over 90% at a near quantitative conversion level. As a control a nonhindered carboxylic acid, *n*-decanoic acid, was also ethoxylated. Under the same reaction conditions: 200 C, one atmosphere pressure, and 0.5 g sodium hydroxide as catalyst/mole of acid, selectivity to monoethoxylate is less than 10% at a comparable high conversion level. The major reaction product is the diester of ethylene glycol with minor amounts of higher ethoxylates.

The high yield of neo-decanoic acid monoethoxylate was found to be quite dependent upon the specific reaction conditions chosen for the ethoxylation. The ratio of the ethylene oxide to neo-acid, for example, is a critical variable. As shown in Fig. 1, it is necessary to terminate the ethoxylation of the presence of, e.g., 1–2% free neo-acid, that is, to stop the reaction at an ethylene oxide/neo-acid molar ratio of somewhat less than 1. If the reaction is permitted to proceed longer with ethylene oxide in excess, diester builds up rapidly to about 40%. Continued ethoxylation ultimately leads to higher ethoxylates as the chief products.

This finding appears to be consistant with the mechanism previously reported for the base-catalyzed reactions of ethylene oxide with fatty acids (1).

$$\mathrm{RCOOH} + \mathrm{HO^-} \xrightarrow{\text{very fast}} \mathrm{RCOO^-} + \mathrm{H_2O} \qquad [5]$$



$$\mathrm{RCOO^-} + \overset{\mathrm{O}}{\mathrm{CH_2{-}CH_2}} \xrightarrow{\text{slow}} \mathrm{RCOOC_2H_4O^-} \qquad [6]$$

TABLE II
Ethoxylation of Neo-Decanoic Acid Effect of Temperature[a]

Temp. C	Time hr	Per cent conv.	Per cent selectivity		
			Mono-ethoxylate	EG diester	Higher ethoxylates
150	9.0	83	86	6	8
200	3.0	98	92	6	2
235	4.5	93	51	48	1

[a] Conditions: 1 Atm, 0.5 g NaOH/mole acid.

TABLE III
Ethoxylation of Neo-Decanoic Acid Effect of Catalyst Concentration[a]

NoOH conc. g/mole	Time hr	Per cent conv.	Per cent selectivity		
			Mono-ethoxylate	EG diester	Higher ethoxylates
0.5	9.0	83	86	6	8
1.0	5.5	99	97	1	2

[a] Conditions: 150 C, 1 Atm.

$$\mathrm{RCOO_2H_4O^-} + \mathrm{RCOOH} \xrightarrow{\text{very fast}} \mathrm{RCOOC_2H_4OH} + \mathrm{RCOO^-} \qquad [7]$$

The initial reaction is believed to proceed through the carboxylate ion which is formed rapidly by reaction with the base [5]. The carboxylate ion then reacts slowly with ethylene oxide to generate the strongly basic alcoholate ion [6] which abstracts a hydrogen from free acid to form monoethoxylate and an additional carboxylate ion for subsequent reaction with ethylene oxide. As the neo-acid is consumed the concentration of the alcoholate ion increases to a point where it catalyzes ester exchange and polyethoxylation.

It is reasonable to assume that nonhindered acids undergo the same sequence of reactions; however, since the ester group [7] is not sterically protected it is more susceptible to ester exchange in the presence of free acid and finite quantities of the alcoholate ion. Resistance to thermal ester exchange is also undoubtedly a factor in explaining the wide differences in diester content noted between branched and straight chain acids (Table I).

Temperature is another critical variable for monoethoxylation. Conversion and selectivity data are shown for three reaction temperatures in Table II. In the temperature range of 150–200 C, high selectivity to monoethoxylate is maintained. But, at temperatures as high as 235 C, selectivity drops to about 50%. Decrease in per cent selectivity may be caused by base-catalyzed ester exchange. A decrease in ethylene oxide solubility in the reaction medium at 235 C may also be indicated by the simultaneous decrease of per cent conversion and per cent higher ethoxylates in spite of longer reaction times. The latter would decrease the monoethoxylate/ethylene glycol diester ratio. As can be seen from reaction times, reaction rate is, as expected, temperature dependent and is quite rapid at 200 C.

Likewise catalyst concentration is an important variable. The effect of varying catalyst concentration at 150 C is shown in Table III. An increase in rate and product selectivity is observed at the higher catalyst level.

The type of ethoxylation catalyst has an even more pronounced effect on product selectivity and conversion. In Table IV data are shown for ethoxylation runs employing sodium hydroxide and sulfuric acid as catalysts; a run using no catalyst is also included. It is quite evident from the data that base is the preferred catalyst. Both the acid-catalyzed and un-

TABLE IV
Ethoxylation of Neo-Decanoic Acid Effect of Catalyst Type[a]

Catalyst	Time hr	Per cent conv.	Per cent selectivity		
			Mono-ethoxylate	EG diester	Higher ethoxylates
NaOH	3.0	98	92	6	2
H_2SO_4 (98%)	4.5	35	12	84	4
None	6.5	29	6	91	3

[a] Conditions: 200 C, 1 Atm, 0.5 g catalyst/mole acid.

TABLE V

Ethoxylation of Straight Chain and Partially Hindered Acids[a]

Acid	Temp. C	Time hr	Per cent conv.	Per cent selectivity		
				Mono-ethoxylate	EG diester	Higher ethoxylates
n-Decanoic	75	17	82	83	13	4
n-Decanoic	100	5	91	46	48	6
2-Ethyl-hexanoic	150	3.0	95	91	5	4
Isobutyric	100	5.0	95	92	8	0
Isobutyric	150	5.5	98	49	49	2

[a] Conditions: 1 Atm, 1.0–3.0 g NaOH/mole acid.

catalyzed ethoxylations give low selectivity to monoethoxylate. Selectivity to ethylene glycol diester, the major reaction product, is in the range of 84–91%. Reaction rates are lower for the latter two cases.

Studies on neo-pentanoic acid (data not given) have also shown selectivity to monoethoxylate of about 90% using base-catalyzed reaction conditions at 150 C.

Additional data for runs on the nonhindered acid, n-decanoic acid, are shown in Table V. Low temperatures favor selectivity to monoethoxylate. Selectivity over 80% is possible at 75 C, but the reaction rate is quite low at this temperature, 17 hr being required for about 80% conversion. Selectivity at 100 C, where rates are faster, is lost.

Dialkylacetic acids were also included in our ethoxylation studies. Results for isobutyric and 2-ethylhexanoic acids are given in Table V. Selectivities to monoethoxylate of over 90% at high conversion levels and rates are observed for these partially hindered acids at temperatures of from 100–150 C. Although 2-ethylhexanoic acid was monoethoxylated in high selectivity at high conversion at 150 C, isobutyric acid was not. This points to increased protection toward ester exchange with increased bulkiness of substitutents on the alpha carbon atom (ethyl vs. methyl).

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