Generation of Maillard-Type Compounds from Triethanolamine Alone

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ABSTRACT: The mechanism of triethanolamine (TEA) soap browning has been uncovered. The reaction proceeds as follows. Firstly, TEA is degraded into diethanolamine and acetaldehyde. Secondly, diethanolamine is further degraded into monoethanolamine and acetaldehyde. Thirdly, two molecules of acetaldehyde dimerize to crotonaldehyde, which reacts with monoethanolamine to generate brownish products with conjugated double bonds. Thus, TEA alone generates Maillard-type products through a series of degradation and recombination reactions.

JAOCS 74, 891–893 (1997).

KEY WORDS: Acetaldehyde, browning, crotonaldehyde, diethanolamine, Maillard reaction, monoethanolamine, soap, triethanolamine.

Soaps are widely used in a variety of household and personal-care products. Quality soaps are triethanolamine (TEA) salts of fats or oils and create quick foaming and dense lather. Also, TEA soaps have good low-temperature solubility. However, when stored at moderately high temperatures (more than 50°C), TEA soaps have been known to acquire a brownish color. If stored for a long period, they gradually show this type of color change at lower temperatures. Colors are appealing to consumers, and discoloration damages products. In this article, we clarified the mechanism in which TEA soaps obtain a brownish color. TEA alone generates Maillard-type products (1–4) through a series of degradation and recombination reactions.

EXPERIMENTAL PROCEDURES

Materials. All reagents were commercially available and were used without further purification.

Qualification and quantitation of amines. A soap solution (2 mL) was mixed with 2 mL of 1M $Na_2CO_3/NaHCO_3$ buffer (pH 9), followed by addition of 100 µL of 12.5% fluorodinitrobenzene/methanol and was incubated at 50°C for 1 h. An aliquot (20 µL) was applied for reversed-phase high-performance liquid chromatography (HPLC) in a C_{18} column (4.6 × 250 mm; Shiseido, Tokyo, Japan); flow rate, 1 mL/min; mobile phase, 0.01% trifluoroacetic acid with increased concentration of methanol from 0 to 80% in 30 min. The chromatographic system was equipped with an ultraviolet detector, and absorbance was read at 350 nm. The analysis was carried out at 30°C.

Qualification and quantitation of aldehydes. A soap solution (1 mL) was mixed with 4 mL of 0.025% dinitrophenylhydrazine/2N HCl and was incubated for 1 h at room temperature. An aliquot (20 µL) was applied for reversed-phase HPLC as described above.

Gas chromatography/mass spectrometry (GC/MS) analysis. All results were obtained with an HP 5972A gas chromatograph/mass spectrometer (Hewlett-Packard, Palo, Alto, CA). Separation of the compounds was achieved on a 15 m × 0.25 mm i.d. methylpolysiloxane (DB-1) fused-silica capillary column (film thickness 0.1 µm) from J&W Scientific (Folsom, CA). Helium was used as a carrier gas at flow rate of 0.55 mL/min. The GC injection port was maintained at 300°C, and the MS interface was maintained at 280°C. The ion source temperature was 280°C. The column oven temperature was raised from 40 to 200°C at 10°C/min and from 200 to 350°C (5 min) at 20°C/min. The mass spectrometer was operated in the scanning mode (range 40–700 *m/z*). Electron ionization was accomplished with electrons with an energy of 70eV. Sample injection was done in the split mode (split ratio 1:30).

RESULTS AND DISCUSSION

When TEA soap is stored at moderately high temperatures (more than 50°C) for a long period (about 1 mon), it gradually acquires a brownish color and a slight odor of aldehyde and amine. We examined the mechanism of this phenomenon. Firstly, we investigated whether TEA soap solution yielded aldehydes and/or amines. Aldehydes were isolated from the solution as their dinitrophenylhydrazones (5) and characterized by C_{18} reversed-phase HPLC. Amines were isolated and characterized as their dinitrophenyl derivatives (6,7) in the same way. When a 5% solution of lauric acid–TEA was stored at 0°C for 1 mon, hardly any aldehyde or amine was detected. However, when the solution was incubated at 50°C, it gradually acquired a brownish color, and acetaldehyde, cro-

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TABLE 1
Quantitative Analysis of Aldehydes and Amines in TEA–Laurate Solution[a]

Incubation	Browning (yes/no)	DEA (ppm)	MEA (ppm)	Acetaldehyde (ppm)	Crotonaldehyde (ppm)
0°C, 1 mon	0	12	<0.5	1	<0.5
50°C, 1 mon	1	530	<0.5	34	13

[a] DEA, diethanolamine; MEA, monoethanolamine; TEA, triethanolamine.

TABLE 3
Assignment of the Peaks by GC/MS[a]

Retention time (min)	M^+	Suggested structure
4.43	185	$CH_3CH{=}CHCH{=}NCH_2CH_2OH$
13.69	370	Cyclodimer
19.00	555	Cyclotrimer

[a] Gas chromatography/mass spectrometry (GC/MS); analyzed as trimethylsilyl derivatives.

tonaldehyde, and diethanolamine (DEA) were detected (Table 1). The mechanism of degradation was considered to be as follows (Scheme 1). TEA was degraded into DEA and vinyl alcohol. Vinyl alcohol was immediately converted into acetaldehyde, and two molecules of acetaldehyde dimerized to crotonaldehyde.

Next, the aldehydes and/or amines (5% H_2O solutions) were reacted in various combinations to see whether brownish compounds would be generated (Table 2). Monoethanolamine (MEA) was tested because it might be generated from DEA in the same way that DEA is generated from TEA. Neither DEA nor acetaldehyde directly afforded brownish compounds, but MEA and crotonaldehyde were essential for the generation of brownish compounds. However, as shown in Table 1, MEA was not detected in the colored lauric acid–TEA solution. There are two possible explanations for this. Firstly, the generated MEA may rapidly react with crotonaldehyde. Secondly, the absolute amount of MEA may be small. As shown in Table 1, the yield of DEA was only 530 ppm from 5% TEA soap solution. If MEA is generated from DEA in the same way that DEA is generated from TEA, the yield of MEA would be very low.

TABLE 2
Combinations of Aldehydes and Amines That Yield Brownish Compounds[a]

	Experiment letter									
	A	B	C	D	E	F	G	H	I	J
MEA	+				+		+	+	+	+
DEA		+			+	+		+	+	
Acetaldehyde			+		+	+	+		+	
Crotonaldehyde				+	+	+	+	+		+
Browning					+		+	+		+

[a] MEA, monoethanolamine; DEA, diethanolamine.

To investigate whether MEA is generated from DEA, 5% lauric acid–DEA soap was prepared and stored at 50°C. The amount of DEA reduced, and MEA was detected in the color-changed DEA–soap solution (data not shown). The results indicate that MEA was generated from DEA, which supports the hypothesis that TEA generated MEA by way of DEA.

Next, MEA was mixed with crotonaldehyde, and the reaction product was analyzed by GC/MS. Crotonaldehyde and MEA were presumed to have undergone the Maillard reaction to afford a compound with conjugated double bonds (Scheme 1), which would easily polymerize (Table 3).

In conclusion, we consider that the browning reaction of TEA soap is a Maillard-type reaction, involving a series of degradation and recombination reactions as shown in Scheme 1: (i) TEA degrades into acetaldehyde and DEA, which further degrades into acetaldehyde and MEA. (ii) Two molecules of acetaldehyde react to afford crotonaldehyde. (iii) Crotonaldehyde reacts with MEA to give a monomer with conjugated double bonds. (iv) The monomer polymerizes to afford products with a molecular weight distribution.

ACKNOWLEDGMENTS

We thank Shinya Yamamoto, Seiichi Yoshida, and Dr. Toshikatsu Hayashi (Shiseido Research Center) for helpful discussions.

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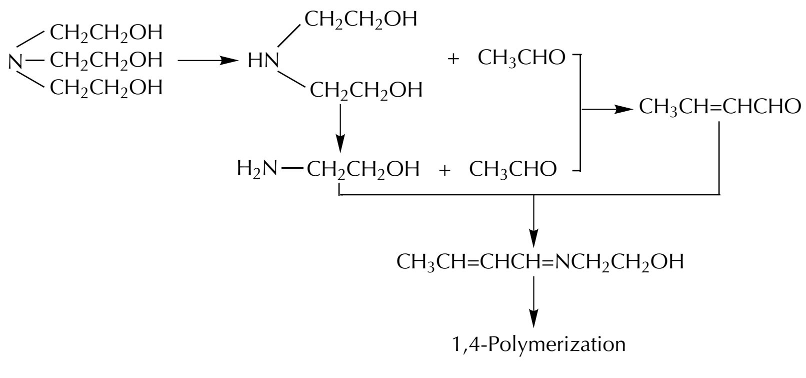

SCHEME 1

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[Received November 19, 1996; accepted March 24, 1997]