

mation of 3,5-dimethyl-1,2,4-trithiolanes at pH = pI.

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**Registry No.** Acetone, 67-64-1; methyl ethyl ketone, 78-93-3; thiophene, 110-02-1; cyclohexene, 110-83-8; thiazole, 288-47-1; 2-methylthiazole, 3581-87-1; 1-mercapto-2-butanone, 39861-37-5; 4,5-dihydro-3(2*H*)-thiophene, 1003-04-9; 2-thiophenethiol, 7774-74-5; 3-thiophenethiol, 7774-73-4; 2-methyl-1,3-dithiolane, 5616-51-3; 2-methyl-5-ethylthiazole, 19961-52-5; 3-methyl-1,2-dithiolane, 55487-20-2; 3-methyl-1,2-dithiolan-4-one, 72771-03-0; 2-acetylthiophene, 88-15-3; 3-methylthiophene-2-carboxaldehyde, 5834-16-2; 2-thiazolyl ethyl ketone, 43039-98-1; 3,5-dimethyl-1,2,4-trithiolane, 23654-92-4; 3-methyl-1,2,4-trithiane, 43040-01-3; 1,2,3-trithia-5-cycloheptene, 13005-82-8; 3,6-dimethyl-1,2,4,5-tetrathiane, 67411-27-2; 2-acetylthiazole, 24295-03-2; 5-methylthiophene-2-carboxaldehyde, 13679-70-4; 2,4,6-trimethyl-1,3,5-dithiazine, 94944-51-1; cysteine, 52-90-4.

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## Volatile Components of the Thermal Degradation of 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone

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2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone or DMHF was subjected to a roasting temperature of 160 °C for 30 min in a closed system at various pH values (2.2, 5.1, and 7.1). The yield of the total volatiles generated decreased with increasing pH value, indicating that degradations occurred more readily at a lower pH. Generally, the volatiles identified were acyclic carbonyls and 3(2*H*)-furanone derivatives, with furanone production favored at the higher pH values. Formation of the described products implies that during thermal degradations in water, DMHF undergoes ring opening and hydrolysis first, then, by a retroaldolization, produces the primary degradation products which react in an intermolecular fashion to form the secondary products. Possible formation mechanisms for the products are postulated.

#### INTRODUCTION

2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone or DMHF has been described as being "burnt pineapple" like and the major "character impact" compound of pineapple flavor concentrate (Rodin et al., 1965). In the flavor industry, this compound is very important due to its pleasant or-

ganoleptic character and has been used extensively for flavoring jams, jellies, beverages, ice creams, alcoholic drinks, and sweets (Hirvi et al., 1980).

DMHF was found in pineapple (Rodin et al., 1965), strawberries (Re et al., 1973), beef broth (Tonsbeek et al., 1968), and roasted almonds (Takei and Yamanishi, 1974) and was also characterized in various model systems such as the degradation of fructose (Shaw et al., 1968), the pyrolysis of D-glucose (Fagerson, 1969; Heyns et al., 1966; Johnson et al., 1969), pyrolysis of 1-deoxy-1-piperidino-D-fructose (Mills et al., 1969), roasting of alanine and rhamnose (Shaw and Berry, 1977), and reactions between rhamnose and piperidinyl acetate (Hodge and Fisher, 1963).

Reports on the stability of DMHF were limited. Hodge et al. (1963) observed that at 25 °C DMHF was very unstable in air and in aqueous solutions. Recently Hirvi

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**Table I. Volatile Components Identified from the Degradation of DMHF at 160 °C and at Different pH Values<sup>a</sup>**

compd identified	GC area, %		
	pH 2.2	pH 5.1	pH 7.1
acetaldehyde	T	T	
acetone	57.3	T	T
methyl ethyl ketone	T		8.9
2,3-butanedione	1.4	2.1	2.5
ethyl acetate		1.9	2.7
hydroxyacetone	T	T	4.2
2,3-pentanedione	12.2	43.9	19.3
acetoin	7.8		
1-hydroxy-2-butanone			T
3-hydroxy-2-butanone		1.5	5.2
2,4-pentanedione		T	
3-hydroxy-2-pentanone	3.1	1.7	9.8
2-hydroxy-3-pentanone	3.0	T	8.8
acetoxyacetone	2.5	10.1	
3-acetoxy-2-butanone	T	2.6	
2,5-dimethyl-3(2H)-furanone	T	T	2.9
2,4,5-trimethyl-3(2H)-furanone <sup>b</sup>	T	2.6	12.5
2-ethyl-5-methyl-3(2H)-furanone <sup>b</sup>		T	
DMHF <sup>c</sup>	T	10.4	6.0
2,4-dimethyl-5-ethyl-3(2H)-furanone <sup>b</sup>		T	T
acetic acid	T		

<sup>a</sup>T = trace, less than 1%. <sup>b</sup>Spectral data from Shu et al., 1980.

<sup>c</sup>Starting material.

et al. (1980) studied the effect of pH on the shelf-life of DMHF at room temperature and found that the optimal stability was at pH 4. However, a study of the degradation products from DMHF has not been reported in the literature. This paper reports the thermal degradation of DMHF at 160 °C, representing the roasting temperature, at three pH values with the emphasis on the degradation products and their formation mechanisms.

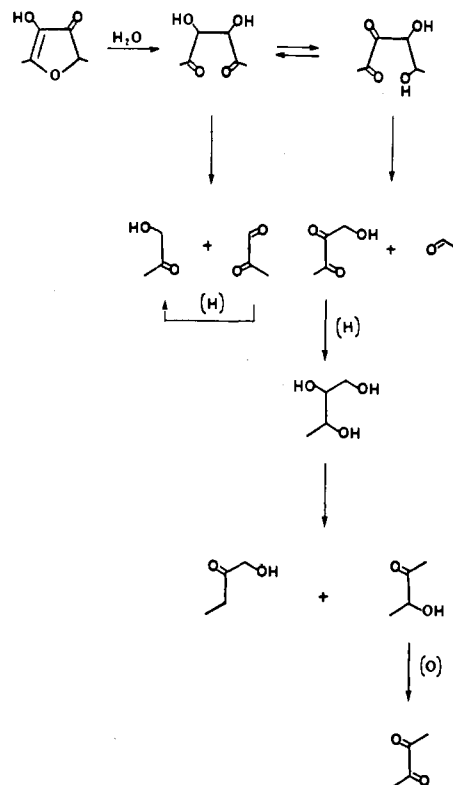
#### EXPERIMENTAL SECTION

As described in another paper (Shu et al., 1984) a 500-g solution was prepared by dissolving 0.05 mol of 2,5-dimethyl-4-hydroxy-3(2H)-furanone (International Flavors and Fragrances) in distilled water; the pH of the solution was measured as 2.2. The solution was placed in a 2-L Parr bomb (Parr Instruments Co., Moline, IL) and heated to 160 °C for 1/2 h. The reaction mass was then vacuum steam-distilled and the distillate extracted with methylene chloride. The extract was concentrated and analyzed by gas chromatography-mass spectrometry (GC-MS). Two other samples were prepared in a similar manner except the initial pH of each solution was adjusted to 5.1 and 7.1 with 10% Na<sub>2</sub>CO<sub>3</sub>.

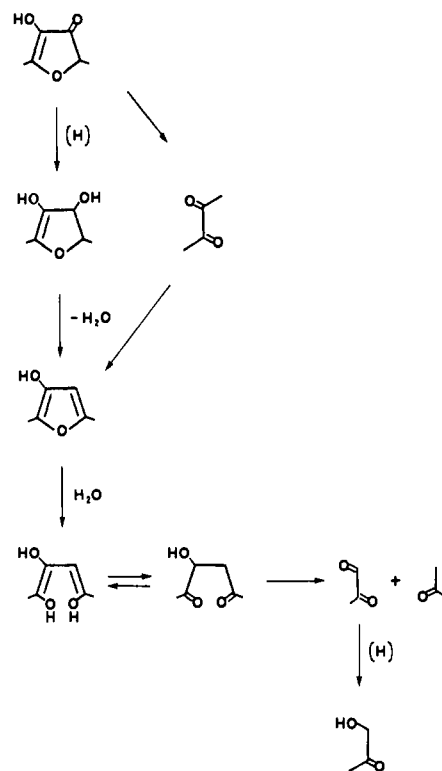
#### RESULTS AND DISCUSSIONS

The yield of the total volatiles from 0.05 mol of DMHF was 175 mg, 130 mg, and 95 mg at pH 2.2, 5.1, and 7.1, respectively, which indicated that degradation of DMHF at 160 °C occurred more readily at lower pH than at higher pH. Table I shows the components identified from the samples prepared at the different pH values, along with the quantitative data (GC area percent).

Table I revealed that most of the degradation products were acyclic carbonyls and the rest were furanones. The results imply that during degradation the ring structure of DMHF opens first to an intermediate, which then undergoes a retroaldolization process to produce a group of primary products, which react in an intermolecular fashion to form secondary products. Figure 1 represents a scheme for the possible formation of the primary products from DMHF including acetaldehyde, hydroxyacetone, 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, and 2,3-bu-

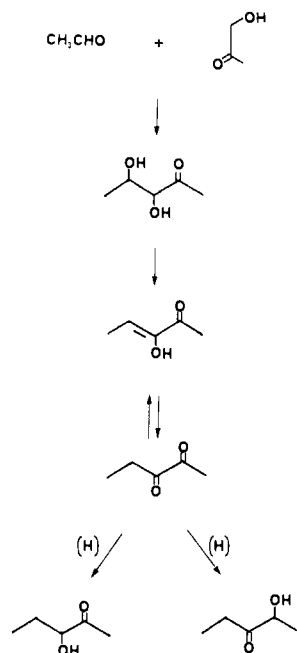


**Figure 1.** The possible formation of the primary degradation products from DMHF.



**Figure 2.** The possible formation of 2,5-dimethyl-3(2H)-furanone and other breakdown products from DMHF.

tanedione. Figure 2 describes the formation of 2,5-dimethyl-(2H)-furanone via reduction/dehydrations or/and via aldol condensation/cyclizations as described by Piloty and Baltes (1979) from which the breakdown products were also derived (acetone and hydroxyacetone). A scheme for the possible formation of the secondary breakdown products is illustrated in Figure 3. Aldol condensation of acetaldehyde and hydroxyacetone (both were primary



**Figure 3.** The possible formation of the secondary degradation products from DMHF.

products) could lead to the formation of 2,3-pentanedione which in turn could be reduced to 3-hydroxy-2-pentanone and 2-hydroxy-3-pentanone.

It is of interest to correlate the major component (2,3-pentanedione) and the three 3(2*H*)-furanone derivatives (2,4,5-trimethyl-, 2-ethyl-5-,methyl-, and 2,4-dimethyl-5-ethyl-3(2*H*)-furanone) which were formed most favorably at the highest pH (7.1). Recently Shu et al. (1980) demonstrated in an independent process that a mixture of four 3(2*H*)-furanones including the three furanones reported here were obtained when 2,3-pentanedione was the starting material. Therefore, the 3(2*H*)-furanones obtained in the degradation of DMHF could likely be derived from 2,3-pentanedione, an intermediate degradation product. The formation mechanism of these furanones is probably similar to the one described by Piloty and Baltes (1979).

**Registry No.** DMHF, 3658-77-3; acetaldehyde, 75-07-0; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; 2,3-butanedione, 431-03-8; ethylacetate, 141-78-6; hydroxyacetone, 116-09-6; 2,3-pentanedione, 600-14-6; acetoin, 513-86-0; 1-hydroxy-2-butanone, 5077-67-8; 3-hydroxy-2-butanone, 513-86-0; 2,4-pentanedione, 123-54-6; 3-hydroxy-2-pentanone, 3142-66-3; 2-hydroxy-3-pentanone, 5704-20-1; acetoxyacetone, 592-20-1; 3-acetoxy-2-butanone, 4906-24-5; 2,5-dimethyl-3(2*H*)-furanone, 14400-67-0; 2,4,5-trimethyl-3(2*H*)-furanone, 64880-73-5; 2-ethyl-5-methyl-3(2*H*)-furanone, 23120-65-2; 2,4-dimethyl-5-ethyl-3(2*H*)-furanone, 74902-72-0; acetic acid, 64-19-7.

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