## **Caustic Fusion of Vanillin**

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Certain variables in the reaction of vanillin with fused caustic alkali to yield either vanillic (4-hydroxy-3-methoxybenzoic) acid or protocatechnic (3,4-dihydroxybenzoic) acid have been studied. Mixtures of potassium and sodium hydroxide containing between 20 and 60% sodium hydroxide proved to be the most suitable for the oxidation reaction. As the percentage of sodium hydroxide increased, the resulting acid became progressively yellower. For the preparation of protocatechnic acid, any mixture of caustic alkalies may be employed, whereas, for the preparation of vanillic acid, the necessity for higher temperatures and/or longer reaction times with high sodium hydroxide ratios invariably results in demethylation and the formation of some protocatechnic acid. Time as well as temperature has been found to play a role in this demethylation reaction. Alkali-vanillin molecular ratios of 4 to 1 and 6 to 1 are necessary for obtaining high yields of vanillic acid and protocatechuic acid, respectively.

EVERAL years ago the transformation of vanillin either to vanillic acid or to protocatechuic acid in high yield by caustic fusion under controlled temperature conditions was described (1). The utility of esters of vanillic acid as nontoxic food preservatives (4), antimicrobic agents (5), and ultraviolet absorbing agents (2) led to a great demand for vanillic acid in the form of its esters by various food, cosmetic, pharmaceutical, medical, and chemical industries, as well as scientific laboratories. To meet this demand, pilot plant production was necessary. The present paper reports the results of several studies on the reaction between vanillin and caustic alkali, the data of which were necessary for the design and operation of a vanillic acid pilot plant.

#### PROTOCATECHUIC ACID IN VANILLIC ACID REACTION MIXTURES

In the earlier investigation (1), it was demonstrated that caustic fusion of vanillin below 240° to 245° C. resulted in very high

yields of vanillic acid free from protocatechnic acid, that fusion of vanillin above 240° to 245° C. yielded protocatechuic acid free from vanillic acid, and that the critical demethylatemperature varied somewhat tion with the alkali-vanillin ratio. Subsequent large-scale experiments on the preparation of vanillic acid by the caustic fusion process indicated that time as well as temperature played a role in the demethylation reaction. Various amounts of protocatechnic acid were obtained along with vanillic acid when fusion mixtures were maintained at temperatures approaching 200° C. for relatively long periods of time. To prove this point the following experiment was performed.

A mixture of 1.52 grams of vanillin and 12 grams of powdered potassium hydrox-ide was placed in a 25-mm. stainless steel

test tube which was heated in a wax bath maintained at 195° to 210° C. A few drops of water were added and the mixture was stirred with a stainless steel thermometer. Reaction commenced when the temperature of the mixture reached 130° C., and the temperature finally rose to approximately bath temperature. Heating was continued for 3 hours, samples were removed occasionally and tested for protocatechnic acid by the very sensitive ferric chloride test. A trace test was evident after 60 minutes and a very strong test was obtained after 135 minutes. After 180 minutes, the melt was cooled somewhat, diluted with water, and acidified with sulfuric acid. The cooled mixture was extracted with ether. The ether was dried and distilled to yield a residue containing 11.4% methoxyl, indicating only 62% vanillic acid in the product.

Thus, it was evident that temperature control was necessary in order to obtain vanillic acid free from protocatechuic acid. A process was evolved for carrying on this oxidation without demethylation. The process is described in the next study.

#### SUBSTITUTION OF CAUSTIC POTASH BY CAUSTIC SODA

Having evolved satisfactory methods for the caustic fusion of vanillin employing caustic potash in the laboratory, a study was made of the possible substitution of the more costly caustic potash by the cheaper caustic soda.

The first series of experiments was on the caustic fusion of vanillin to yield vanillic acid using the arbitrary ratio of caustic alkali to vanillin employed in the earlier work (1), but substituting varying amounts of sodium hydroxide for the potassium hydroxide. Eleven experiments were made in this series, beginning with 100% potassium hydroxide and substituting 10% of the caustic by sodium hydroxide in each successive experiment until 100% sodium hydroxide was used. Each experiment was made with 152 grams (1.0 mole) of vanillin and 416 grams of caustic. The composition of the caustic mixture was determined on a weight basis, disregarding molecular weights. The potassium and sodium hydroxides employed contained 85% potassium hydroxide and 97% sodium hydroxide, respectively. All experiments were performed in an identical manner within the limits

	TABLE I.	VANILLIC .	ACID PR	EPARATIONS
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			T 1111			TROTD T		110105			
Expt.	KOH, G.	Na G.	OH %	Max. Temp., ° C.	Preci G.	M.p.,	Ether G.	Extractb M.p., °C.	Tot Yie G.	al Id %	Re- marks <sup>e</sup>
1 2 3 4	416 374 332 291	0 42 84 125	0 10 20 30	195 188 198 200	$146 \\ 140 \\ 147 \\ 156$	$208 \\ 210 \\ 210 \\ 210 \\ 210$	5 6 5 5	175 173 178 180	$151 \\ 146 \\ 152 \\ 161$	90 87 90 96	$1 \\ 2 \\ \cdots$
5 6 7 8	$250 \\ 208 \\ 166 \\ 125$	$166 \\ 208 \\ 250 \\ 291$	40 50 60 70	$200 \\ 206 \\ 194 \\ 192$	$157 \\ 154 \\ 150 \\ 146$	$210 \\ 210 \\ 210 \\ 210 \\ 210$	$\begin{smallmatrix}&&6\\10\\&&6\\&5\end{smallmatrix}$	181 178 180 177	$163 \\ 164 \\ 156 \\ 151 $	97 98 93 90	3
9 10 11d	$\substack{\substack{84\\42\\0}}$	$332 \\ 374 \\ 416$	80 90 100	$208 \\ 206 \\ 186$	$126 \\ 97 \\ 0$	205 206	$\begin{smallmatrix}12\\8\\7\end{smallmatrix}$	$184 \\ 183 \\ 193$	$\substack{138\\105}{7}$	$\substack{ 82\\63\\4 }$	 4

a Negative test for protocatechuic acid in all cases except experiment 11 for which there was no

precipitate. b Test for protocatechuic acid showed a trace in experiments 1 to 5 and 7 to 8; positive in 6, 9, and 10; negative in 11.
 As NaOH ratio increased in successive experiments, the color of the precipitate became progressively

<sup>6</sup> As NaOH ratio increased in successive experiments, the color of the precipitate became progressively more yellow. 1, heavy white precipitate separated, see *a*; 2, low maximum temperature shows incomplete reaction—low total yield; 3, high maximum temperature indicating start of second reaction—greater ether extract showing positive test for protocatechnic acid; 4, additional 500 ml. of H<sub>2</sub>O needed to bring the material into solution.
<sup>d</sup> In this experiment it was necessary to depart slightly from standard procedure because of incomplete reaction obtained. Reaction was so incomplete that most of the product was unchanged vanillin. Entire product was redissolved in dilute NaOH solution, acidified with SO2, and extracted with ether. The ether extract was dried and distilled, leaving only a small amount of vanillic acid. Vanillin was recovered from the bisulfite solution.

TABLE IL

PROTOCATECHILIC ACID PREPARATIONS

		Fusion 3	Mixture											
Expt.	KOH,	Na G.	<u>он</u> %	Melting temp., °C.	React	tion Temp II	.ª, °C. III	Precip G.	M.p., °C.	Ether I G.	Extract <sup>e</sup> M.p., °C.	Yield G.	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Remarksd
1 2 3 4 5 6 7	$\begin{array}{c} 416\\ 374\\ 332\\ 291\\ 250\\ 208\\ 166\\ 166\\ 166\end{array}$	0 42 84 125 166 208 250	0 10 20 30 40 50 60	165 120 120 120 120 120 120 120 130	208 198 204 198 204 200 210	220 210 215 215 220 220	250 250 250 250 250 250 250	105 100 94 102 109 85 108	202 201 201 198 197 202 196	48 53 59 50 43 65 45	180 192 194 191 187 192 183	153 153 153 152 152 152 150 153	99 99 99 99 99 99 99 98 99	1¢ 2 2 3 3 3
8 9 <i>1</i>	84	291 332	70 80	140	200	$\frac{220}{230}$	$250 \\ 250$	51 58	192 194	93 78	195 188	144 58 g., 34% h 78 g., 51% g	93 85	3 4
105	42	374	90	165	190	230	260	120	202	41	191	120 g., 72% h 41 g., 26% g	98	4
124	42	374	<b>90</b>	170	178	220 220	230 275	31	204 188	04 121	193 194	54 g., 35% 152	<b>89</b> 99	4 5

124 42 374 90 170 185 220 275 31 188 121 194 152 99 5 a I, maximum temperature of the first reaction; II, temperature at which the second reaction began; III, maximum temperature attained. b Positive test for protocatechuic acid except in experiments 9 to 11. c Positive test for protocatechuic acid except in experiments 9 to 11. c Positive test for protocatechuic acid accept in experiments 9 to 11. c Positive test for protocatechuic acid accept in experiments 9 to 11. c Positive test for protocatechuic acid accept in experiments 9 to 11. c Positive test for protocatechuic acid accept in experiments 9 to 11. c Positive test for protocatechuic acid accept in experiments 9 to 11. c Positive test for protocatechuic acid in all cases. d 1, ppt. light and very pure, ether extract quite dark and impure; 2, fluffy ppt., settled out slowly; 3, crystalline ppt., settled out slowly; 4, fluffy ppt., settled out at once; 5, flaky ppt., settled out slowly. d As percentage of NaOH increased in successive experiments, the precipitate became darker in color; the ether extract became lighter in color with in-creased NaOH. J In experiments 9, 10, and 11, reactions were not complete and, therefore, both vanillic acid and protocatechuic acid appeared in the product. When employing as much as 80% NaOH in the caustic mixture, a higher temperature and/or longer reaction time are needed to give complete reaction (see experi-ment 12 and 4). The percentage of vanillin recovered as vanillic and protocatechuic acid. The original fused caustic at 165° to 170° C. still contained solid caustic in suspension. Protocatechuic acid. A Vanillic acid. A Vanillic acid. A Vanillic acid. A Vanillic acid. A Wanillic acid. A Wanillic acid. A Mith continued heating, the second reaction began at approximately 220° C. The temperature was increased to 275° C., maintained there for 10 minutes, and mixture allowed to cool.

of experimental technique and several uncontrollable factors, such as the maximum temperature reached by the reaction mixture, the fluidity of the caustic mixture before vanillin addition, and the condition of the reaction mixture after reaction was complete.

The procedure employed in all experiments was as follows:

A mixture of the caustic and 50 ml. of water was placed in a stainless steel beaker heated by a heavy duty electric hot plate. A heavy duty Lightnin' mixer was used for stirring. The caustic mixture was heated with stirring to 165° C., at which time the electric hot plate was turned off and 152 grams of vanillin were added slowly with stirring. The rate of vanillin addition was adjusted so that the heat of reaction did not raise the tempera-ture of the reaction mixture much above 200° C. After all the vanillin had been added the mixture was stirred an additional vanillin had been added, the mixture was stirred an additional 5 minutes, cooled slightly, and dissolved in 1500 ml. of water. The alkaline solution was given a flash treatment with sulfur dioxide (to prevent the formation of colored products when hydrochloric acid is added later) and acidified with hydrochloric acid. The precipitate was filtered, washed with cold water, and The combined filtrate and washings were extracted with dried. The ether was dried and distilled, leaving a solid product. ether.

The results of the eleven experiments in this series are given in Table I and Figure 1.

An analogous series, comprising eleven experiments, was made on the caustic fusion of vanillin to protocatechuic acid. As

before, all experiments were performed in as identical a manner as possible. A mixture of the caustic and 50 ml. of water was heated with stirring to 165° C., at which point the vanillin was slowly added. After reaction was complete, the temperature was raised to 250° C. and maintained there for 1 hour. The mixture was cooled somewhat, dissolved in 1500 ml. of water, and treated as described under the vanillic acid series. Results are given in Table II and Figure 1.

The results on the replacement of a part of the potassium hydroxide by varying amounts of sodium hydroxide in the caustic fusion of



Sodium Hydroxide, % Figure 1. Caustic Fusion of Vanillin with Varying Percentages of Sodium and Potassium Hydroxides

T.	ABLE I	II. VARIA	TIONS I	N VANILI	ли-Роз	rassium 1	Iydro	XIDE RAT Yield	10
			Prec	ipitate <sup>a</sup>	Ether	Extract <sup>5</sup>	•	Basis of	Basis of vanillin
Experi- ment	$\frac{KOI}{G.}$	H (85%) Moles	G.	M.p., ° C.	G.	M.p., °C.	G.	vanillin, %	reacted,
$1 \\ 2 \\ 3$	$198 \\ 211 \\ 224$	$3.0 \\ 3.2 \\ 3.4$	$130 \\ 130 \\ 132$	c d 209	$25 \\ 25 \\ 21$	74 73	$28 \\ 55 \\ 132$	17 33 79	99 97 91
4 5 6	$231 \\ 264 \\ 271$	$\substack{\textbf{3.5}\\\textbf{4.0}\\\textbf{4.1}}$	137 138 138	207 210 208	21 21 21	74 73 74	137 138 138	82 82 82	94 95 95
7 8 9	$277 \\ 280 \\ 336$	$\substack{\textbf{4.2}\\\textbf{4.25}\\\textbf{5.1}}$	$135 \\ 143 \\ 146$	$208 \\ 210 \\ 210$	21 20 17	72 75 74	$135 \\ 143 \\ 146$	80 85 87	92 98 98

<sup>a</sup> Product was vanillin and vanillic acid for experiments 1 and 2, and vanillic acid for 3 to 9.
<sup>b</sup> Product was vanillin in all cases.
<sup>c</sup> Precipitate yielded 28 g. vanillic acid, m.p. of 210° C.; ether extract yielded no acid.
<sup>d</sup> Precipitate yielded 55 g. vanillic acid, m.p. of 210° C.; ether extract yielded no acid.

TABLE IV. VARIATIONS IN MIXED ALKALI-VANILLIN RATIO

	Caustic					Max.		Precipitate	ı		Ether Extrac			
Experi- ment	$\frac{KOH}{G}$	(85%) Moles	G.	H (97%) Moles	Total, moles	Temp., °C.	G.	Product	M.p., ° C.	G.	Product	M.p., °C.	G.	eld %
1 2 3 4	$76 \\ 89 \\ 102 \\ 115$	$1.2 \\ 1.4 \\ 1.5 \\ 1.7$	$76 \\ 89 \\ 102 \\ 115$	$1.8 \\ 2.1 \\ 2.5 \\ 2.8$	$3.0 \\ 3.5 \\ 4.0 \\ 4.5$	180 186 182 193	$142 \\ 146 \\ 152 \\ 154$	I, II I, II II II	202 206	$21 \\ 21 \\ 14 \\ 8$	I, II I, II I I	 74	$8\\61\\152\\154$	58 36° 90 92
5 6 7 8	$127 \\ 152 \\ 178 \\ 208$	$1.9 \\ 2.4 \\ 2.7 \\ 3.2$	$127 \\ 152 \\ 178 \\ 208$	$3.1 \\ 3.6 \\ 4.3 \\ 5.0$	$5.0 \\ 6.0 \\ 7.0 \\ 8.2$	$194 \\ 196 \\ 197 \\ 205$	$155 \\ 162 \\ 161 \\ 154$	II II II II	$205 \\ 209 \\ 210 \\ 210 \\ 210 \\$	$\begin{array}{c}10\\6\\10\end{array}$	I, II I, II I, III I, III I, III	143 184 178	$156 \\ 164 \\ 167 \\ 164 \\ 164$	93 98 99 98

I, vanillin; II, vanillic acid; III, protocatechuic acid.
 Precipitate yielded 5 g. acid, m.p. of 201° C.; extract yielded 3 g., m.p. of 210° C.
 Precipitate yielded 55 g., m.p. of 210° C.; extract yielded 6 g., m.p. of 210° C.

TABLE V.	VARIATIONS IN	VANILLIN-ALKALI RATI	OS IN PROTOCATECHUIC ACID
		PREPARATIONS	

	Caustic			Caustic Max. Precipitate						Ether Extract <sup>e</sup>				
Experi- ment	NaOH, g.	KOH, g.	Total, moles	Temp., °C.	G.	%	M.p., ° C.	G.	%	M.p., ° C.	G.	1d b		
1 2 3	0 0 0	$330 \\ 363 \\ 416$	$5.0 \\ 5.5 \\ 6.3$	$244 \\ 252 \\ 250$	$75 \\ 78 \\ 105$	$\frac{51}{68}$	$^{174o}_{198}_{202}$	$78 \\ 75 \\ 48$	$51 \\ 48 \\ 31$	$188 \\ 192 \\ 180$	$153 \\ 153 \\ 153$	99 99		
4 5 6 7	$127 \\ 152 \\ 178 \\ 208$	$127 \\ 152 \\ 178 \\ 208$	$5.0 \\ 6.0 \\ 7.0 \\ 8.2$	$274 \\ 268 \\ 252 \\ 250$	$74 \\ 103 \\ 80 \\ 85$		172° 195 198 202	$78 \\ 50 \\ 73 \\ 65$	$51 \\ 32 \\ 47 \\ 43$	$190 \\ 181 \\ 186 \\ 192$	$152 \\ 153 \\ 153 \\ 150 $	99 99 98		

<sup>a</sup> Only protocatechnic acid was obtained from the ether extract.

Percentage given only in cases where entire product is protocatechuic acid.
 Vanillic acid present in precipitate.

vanillin as given in Tables I and II indicated a number of facts:

1. The workability of the caustic mixture increases with sodium hydroxide addition and the mixture remains workable until the sodium hydroxide percentage (by weight) approaches 70. The caustic mixtures which proved the most workable in the laboratory contained between 20 and 60% sodium hydroxide.

2. As the percentage of sodium hydroxide was increased above 60, the temperature and/or the time of reaction had to be increased.

3. Increased sodium hydroxide ratios resulted in slightly yellower products. However, the purity of the product was not noticeably reduced.

4. For the preparation of protocatechnic acid, any mixture of caustic alkalies may be used whereas, for the preparation of vanillic acid, the necessity for higher temperatures and/or longer reaction times with high sodium hydroxide ratios invariably results in the formation of some protocatechuic acid.

#### CHANGES IN ALKALI-VANILLIN RATIO

VANILLIC ACID. In the above series, 152 grams of vanillin were fused with 416 grams of alkali. In the case of potassium hydroxide (85%) alone, the molecular ratio for alkali-vanillin amounted to 6.3 to 1. The next study comprised a series of experiments in which vanillin was fused under vanillic acidyielding conditions, with varying mole ratios of potassium hydroxide, in an effort to determine whether the alkali-vanillin ratios could be decreased.

The procedure employed in all experiments was that described above, 1 mole of vanillin being used. In all cases, the small amount of ether extractives isolated consisted essentially of vanillin. The results of this study are found in Table III and Figure 2. The percentage yields of vanillic acid noted in Figure 2 are calculated on the basis of the vanillin used in the experiment (152 grams). In Table III, an additional column is included. giving the percentage of vanillic acid calculated on the vanillin actually consumed in the reaction. In Figure 2, the point for 6.3 moles of potassium hydroxide was taken from Table I.

From these data, it is easily seen that the yield of vanillic acid drops rapidly when the ratio of potassium hydroxide to vanillin

falls below 3.3 to 1. Later evidence has shown that all yields could be raised somewhat by slightly longer reaction times. Vanillin recoveries are thus correspondingly lowered.

In Table I it was shown that the highest yield of vanillic acid (98%) was obtained when a 50 to 50 mixture (by weight) of sodium and potassium hydroxide was employed. In that experiment the total moles of alkali used amounted to 8.2. The next series of experiments was one in which vanillin was fused with a 50 to 50 weight mixture of potassium

and sodium hydroxides, but with varying alkali-vanillin ratios.

All experiments were performed with 1 mole of vanillin as described above. In those experiments in which vanillin was obtained in the product, the material was dissolved in dilute sodium hydroxide and acidified with sulfur dioxide. Only the vanillie acid would precipitate. The results of this series are found in Table IV and Figure 2. These data indicate that high yields of



Figure 2. Variations in Alkali Hydroxide-Vanillin Ratio

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vanillic acid can be obtained only when 4 or more moles of mixed alkali are employed for each mole of vanillin. As in the last series, later evidence has shown that all yields could be raised somewhat by slightly longer reaction times.

PROTOCATECHUIC ACID. Two series similar to the last two were made under the protocatechuic acid-yielding conditions described earlier. The data for the two series have been combined in Table V. The first three experiments, employing potassium hydroxide alone, indicated that 5.5 moles of potassium hydroxide per mole of vanillin is about the lowest alkali-vanillin ratio which will give satisfactory results.

The data for the next four experiments, employing 50 to 50 mixed alkali, indicated that an alkali-vanillin ratio of 6 to 1 is the lowest ratio which gives good results and a pure product in the oxidation of vanillin to protocatechuic acid with the 50 to 50 caustic mixture.

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# Salt Effect in Vapor-Liquid Equilibria

## ETHANOL-WATER SATURATED WITH POTASSIUM NITRATE

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Vapor-liquid equilibrium data have been obtained for the system ethanol-water saturated with potassium nitrate at atmospheric pressure. A large increase in the relative volatility was observed at low ethanol concentrations. The effect of the presence of the salt on the activity coefficients of the two liquid components is illustrated and discussed. The possibility is suggested that salts may be added to many mixtures which are to be distilled in order to improve the separation factor.

HE problem of solvent recovery from a solution containing salts arose as part of a program (12) to investigate the possibilities of industrial crystallization of inorganic salts by means of organic precipitants such as the common alcohols. To be economically feasible the solvent must be recovered as completely as possible and to estimate the distillation requirements, the vapor-liquid equilibrium data are necessary for the system under consideration. The addition of a solid substance to a system of two liquid components will affect the solubilities and partial vapor pressures of the two liquids. If the salt is very soluble in one liquid component but not in the other, their mutual solubilities are decreased (4), and the vapor pressure of the liquid in which the salt is soluble will be decreased while that of the other component will not be appreciably affected (14). From the standpoint of distillation, this means that the liquids in a system of this type would be easier to separate than if the salt were not present.

As little has been published on the exact effect of dissolved salts on the vapor-liquid equilibria of common mixtures, it was felt that quantitative data of this nature would be valuable. Solutions saturated with salt were used because it was expected that maximum influence would be exerted and also because solutions obtained for solvent recovery in the precipitation method of

<sup>1</sup> Present address, Eastern Regional Research Laboratory, Philadelphia 18, Pa. crystallization would be saturated with salt. The system ethanol-water was chosen as the equilibrium data for this system are well known (1, 2, 7, 10, 11); this system was used in some of the work on crystallization, and accurate density-composition data are available (6, 9). Potassium nitrate was used because it is very soluble in water and only slightly soluble in ethanol and because the density of saturated solutions of this salt in aqueous ethanol had been accurately determined (13).

#### EQUILIBRIUM DATA FOR AQUEOUS ETHANOL SOLUTIONS

The vapor-liquid equilibrium data for the binary ethanol-water system have been very thoroughly investigated by several experimenters. Carey and Lewis (1, 10) used an Othmer-type still (7); Cornell and Montonna (2) used differential-type distillation; Jones, Schoenborn, and Colburn (5) used a new still of their own design; and Rieder and Thompson (11) used a Gillespie still (3). On the whole, the data of these investigators show good agreement. All the stills mentioned incorporate various features of design to minimize refluxing and fractionation of the vapor sample or entrainment of the boiler liquid into the vapor. The Othmer-type still was chosen for these experiments because it proved most satisfactory for handling ethanol-water solutions saturated with salt.

#### EQUIPMENT AND EXPERIMENTAL TECHNIQUE

The equilibrium still used for these experiments was a slightly modified Othmer-type (7, 8), heated by an electric radiant heater placed underneath. The walls of the still were kept at or above the boiling temperature by Nichrome wire embedded in lagging on the walls and on the straight section above the still pot. The modifications consisted of a smaller condensate chamber and a 10-mm. bore, heated sampling stopcock set about 35 mm. above the bottom of the still pot.