Study of the Steam Distillation of Phenolic Compounds Using Ultraviolet Spectrometry

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The steam distillation of 42 phenolic compounds was studied by use of a semimicro steam distillation apparatus and ultraviolet spectrometry. In the distillation, the following gave recoveries greater than 95%: phenol, 2-nitrophenol, 2-methoxyphenol, 2-bromophenol, 2-chlorophenol, 2,3- and 2,4-dichlorophenol, 2,4,5- and 2,4,6-trichlorophenol, 2,4-dibromophenol, 2-, 3-, and 4-methylphenol, 4-chloro-2-methylphenol, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylphenol, 4-*tert*-butylphenol, 4-*tert*-amylphenol, thymol, and carvacrol. The percent recovery for the other phenolic compounds was as follows: 3-nitrophenol, 3.7%; 4-nitrophenol, 1.8; 3-methoxyphenol, 31.1; 4-methoxyphenol, 23.2; 3-bromophenol, 79.6; 4-bromophenol, 67.8; 3-chlorophenol, 93.5; 4-chlorophenol, 91.6; 3,4-dichlorophenol, 64.1; 2,4-dinitrophenol, 21.2; 2,4,6-trinitrophenol, 0.0; 2-aminophenol, 0.1; 3-aminophenol, 0.2; 4-aminophenol, 0.1; pyrocatechol, 1.6; resorcinol, 0.4; hydroquinone, 0.0; pyrogallol, 0.7; and phloroglucinol, 0.1. By the examination of the spectra of the undistilled, distilled, and residual solutions, it is concluded that the aminophenols undergo some decomposition and the hydroquinone is almost completely destroyed during the distillation. The important role that hydrogen bonding (intermolecular and intramolecular) plays in the recovery in the steam distillation is examined.

Although steam distillation is frequently used as a means of separation prior to the determination of total phenolic compounds (*1*, *2*), there is a surprising lack of quantitative data on the extent of volatilization of phenolic compounds in a steam distillation (aside from phenol). Even qualitative data are very scant (*3*–*5*). It is the purpose of the present paper to study the steam distillation of phenolic compounds by use of a semimicro steam distillation apparatus and ultraviolet spectrometry.

EXPERIMENTAL SECTION

Apparatus and Reagents. A Varian Cary 219 spectrophotometer and a semimicro steam distillation apparatus of the Parnas-Wagner type with a Liebig condenser (28 cm in length and 20 mm o.d.) were used.

All the reagents were reagent grade. The phenolic compounds were obtained from Eastman Kodak Co. or Aldrich Chemical Co.

Preparation of Standard Solutions. Standard solutions (~2 mg/mL) of phenol, 2-, 3-, and 4-nitrophenol, 2-, 3-, and 4-methoxyphenol, 2-, 3-, and 4-bromophenol, 2-, 3-, and 4-chlorophenol, 2-, 3-, and 4-methylphenol, 4-chloro-2-methylphenol, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylphenol, 4-*tert*-butylphenol, 4-*tert*-amylphenol, thymol, carvacrol, 2,3-, 2,4-, and 3,4-dichlorophenol, 2,4,5- and 2,4,6-trichlorophenol, 2,4-dibromophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 2-, 3-, and 4-aminophenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, and phloroglucinol were prepared by dissolution of about 0.20 g (weighed to 0.1 mg) in 50 mL of methanol, washing into a 100-mL volumetric flask with methanol, and dilution to the mark with water. The solutions of the aminophenols, pyrocatechol, resorcinol, hydroquinone, pyrogallol, and phloroglucinol were prepared fresh daily. The remaining solutions are stable for at least 2 weeks if they are stored in brown bottles.

Study of the Distillation Procedure. The spectra of the phenolic compounds were obtained after pipetting a 2.00-mL aliquot of the standard solutions (equivalent to about 4 mg of the compound) into 100-mL volumetric flasks, adding about 50 mL of water and 2.0 mL of 1 N hydrochloric acid, and diluting to the mark with water. For the mono-, di-, and trinitrophenols, the dilutions were made in 250-mL volumetric flasks after adding 5.0 mL of 1 N hydrochloric acid. For the distillation studies, a 2.00-mL aliquot of the standard solution was pipetted into a 50-mL beaker and 20 mL of water added, followed by 2 drops of sulfuric acid (1 to 9) from a dropping bottle. The solution was decanted through the entry funnel into the distillation flask and the beaker and entry funnel were washed with water. A 100-mL volumetric flask containing 10 mL of water was placed under the exit tube so that the tube reached to the bottom of the volumetric flask. The sample was distilled until the volume in the volumetric flask (counting the washings) was 90–95 mL. Then, 2.0 mL of 1 N hydrochloric acid was added, the solution diluted to the mark, and the spectrum recorded (for 2-nitrophenol, the solution was diluted to 250 mL after adding 5.0 mL of 1 N hydrochloric acid). In most cases, the spectrum of the residual solution left after the distillation was obtained after draining the solution into a 100-mL volumetric flask, adding 2.0 mL of 1 N hydrochloric acid, and diluting to the mark with water. The percent phenolic compound recovered was determined by comparison of the absorbances with and without distillation.

RESULTS AND DISCUSSION

Ultraviolet Spectra of Phenolic Compounds. The solutions on which the ultraviolet spectra are run should be acidic in order to ensure, where possible, that the phenolic compound is in the enolic form and not the anionic form. The acidity is not critical. For phenol, the same curves were obtained over the range 0.1–25 mL of 1 N hydrochloric acid per 100 mL. Two milliliters of 1 N hydrochloric acid per 100 mL is recommended. The ultraviolet spectra of phenolic compounds usually show a very large peak in the vicinity of about 210–220 nm and a smaller peak (or peaks) at a higher wavelength. The large peak was deemed too sensitive to study the distillation process, so the peak at the higher wavelength was chosen. This peak ordinarily gave an absorbance of about 0.4–1.2 for a solution containing 4 mg of the phenolic compound per 100 mL. However, the sensitivities for the mono-, di-, and trinitrophenols were much greater and for these compounds the dilution was made to 250 mL (after adding 5 mL of 1 N hydrochloric acid).

Study of the Distillation Process. The acidity for the distillation is not critical, providing that the pH of the solution is less than about 4. The pH of the solution after adding the 2 drops of sulfuric acid (1 to 9) was about 2.0. Most of the phenolic compound comes over during the first few minutes of the distillation.

The wavelength of maximum absorption (λ_{max}) of the peak in the undistilled sample, the millimolar absorptivity ($m\epsilon$) of this peak, and recovery of the phenolic compound in the distilled sample are shown in Table I.

For all the samples except the aminophenols and hydroquinone, the total of the phenolic compound in the distillate and residual solution was reasonably close to 100% and there

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Table I. Study of the Steam Distillation of Phenolic Compounds

compound	undistilled sample: λ_{max}, nm	undistilled sample: absorptivity, mε	% recovery, distilled sample
phenol	271	1.64	95.3
2-nitrophenol	278	6.52	99.9
3-nitrophenol	273	6.90	3.7
4-nitrophenol	317	9.99	1.8
2-methoxyphenol (guaiacal)	274	2.20	100.2
3-methoxyphenol	273	1.77	31.1
4-methoxyphenol	287	2.54	23.2
2-bromophenol	274	2.07	100.3
3-bromophenol	274	1.81	79.6
4-bromophenol	280	1.40	67.8
2-chlorophenol	273	1.89	99.9
3-chlorophenol	274	1.65	93.5
4-chlorophenol	280	1.43	91.6
2-methylphenol	270	1.62	100.1
3-methylphenol	271	1.45	100.4
4-methylphenol	277	1.74	100.0
4-chloro-2-methylphenol	280	1.73	99.8
2,4-dimethylphenol	277	1.85	100.1
2,5-dimethylphenol	274	1.79	100.0
2,6-dimethylphenol	269	1.23	99.8
3,4-dimethylphenol	277	1.81	99.6
3,5-dimethylphenol	272	1.19	100.1
4-*tert*-butylphenol	274	1.58	100.0
4-*tert*-amylphenol	275	1.54	99.9
thymol (5-CH_3-2-[$(CH_3)_2CH$]-C_6H_3-1-OH)	274	1.99	100.4
carvacrol (2-CH_3-5-[$(CH_3)_2CH$]-C_6H_3-1-OH)	275	1.59	100.1
2,3-dichlorophenol	276	1.84	99.8
2,4-dichlorophenol	284	2.12	99.7
3,4-dichlorophenol	283	1.83	64.1
2,4,5-trichlorophenol	289	2.68	99.3
2,4,6-trichlorophenol	287	2.24	99.8
2,4-dibromophenol	285	2.12	100.2
2,4-dinitrophenol	261	11.9	21.2
2,4,6-trinitrophenol	355	10.6	0.0
2-aminophenol	270	2.01	0.1[a]
3-aminophenol	270	1.87	0.2[b]
4-aminophenol	272	1.65	0.1[c]
pyrocatechol (1,2-$(HO)_2C_6H_4$)	275	2.34	1.6[d]
resorcinol (1,3-$(HO)_2C_6H_4$)	273	1.76	0.4[e]
hydroquinone (1,4-$(HO)_2C_6H_4$)	288	2.65	0.0[f]
pyrogallol (1,2,3-$(HO)_3C_6H_3$)	266	0.73	0.7[g]
phloroglucinol (1,3,5-$(HO)_2C_6H_3$)[i]	267	0.46	0.1[h]

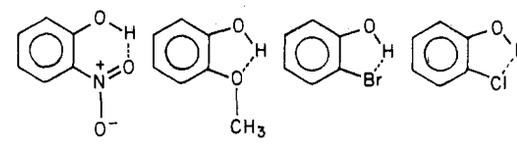
[a] Some decomposition; 92.5% recovery in residual solution (peak at 270 nm); new peak in distillate at 259 nm (A = 0.079). [b] Some decomposition; 95.2% recovery in residual solution (peak at 270 nm). [c] Some decomposition; 92.6% recovery in residual solution (peak at 271 nm); new peak in distillate at 245 nm (A = 0.137). [d] 98.2% recovery in residual solution (peak at 275 nm). [e] 99.5% recovery in residual solution (peak at 273 nm). [f] Considerable decomposition; 0.8% recovery in residual solution (peak at 287 nm); new peak in distillate at 246 nm (A = 0.135); new peaks in residual solution at 268 nm (A = 0.077) and at 277 nm (A = 0.089). [g] 99.2% recovery in residual solution (peak at 266 nm). [h] 99.3% recovery in residual solution (peak at 266 nm). [i] Added as 1,3,5-$(HO)_3C_6H_3 \cdot 2H_2O$.

were no new peaks. With the aminophenols, the total was 92.6–95.4% and there were new peaks in the distillate (for the 2- and 4-aminophenol samples), indicating some decomposition (Table I). With the hydroquinone, the total was 0.8% and there were new peaks in both the distillate and residual solution, indicating almost complete decomposition (Table I). The air in the system is driven out very early in the distillation, so it is believed that the decompositions are due to thermal and hydrolytic reactions, rather than oxidation by air.

Role of Hydrogen Bonding. A factor that has great influence on the extent of volatilization of a phenolic compound in the steam distillation is hydrogen bonding. As has been indicated in the treatises by Pimental and McClellan (*6*) and Vinogradov and Linnell (*7*), hydrogen bonding has been correlated with many of the properties of organic compounds, such as molecular weight, molar volume, melting point, boiling point, solubility, dielectric properties, ionization, polarographic reduction potential, refractive index, viscosity, adsorption (chromatography), reaction rates, and infrared, electronic, and NMR spectra. However, very little has been reported in the literature on the effect of hydrogen bonding on the recovery in steam distillation, except mention that 2-nitrophenol can be separated from 3- and 4-nitrophenol by steam distillation because of the intramolecular hydrogen bonding of 2-nitrophenol (*3–5*).

The linkages that would be involved in hydrogen bonding in phenols would be O–H···O and O–H···halogen. There are two types of hydrogen bonding, namely intermolecular and intramolecular (*6, 7*). Intermolecular hydrogen bonding involves linkage with other molecules of the compound or linkage between molecules of the compound and molecules of water. In aqueous solution, chains and rings are produced involving many molecules of the compound and many molecules of water.

Intramolecular bonding in phenolic compounds occurs when spatial arrangements in the molecule permits the hydroxyl group to form a hydrogen bond with an adjacent nitro, ether oxygen, or halogen group as indicated in the following formulas:



Molecules with intramolecular hydrogen bonding have properties that are about equal to those of nonbonded molecules of similar size and shape, while molecules with intermolecular bonding behave abnormally as a result of their association with other molecules and water. This difference in behavior of the two types of hydrogen bonding explains why practically complete recovery is obtained in the steam distillation with the ortho isomers of nitro-, methoxy-, bromo-, and chlorophenol and only partial recovery with the meta and para isomers. In going from the ortho to the meta to the para isomers of the above compounds, there is a stepwise decrease in recovery (Table I). The total decrease in recovery (%) in each series in going from the ortho to the para compound is as follows: nitrophenols, 98.1; methoxyphenols, 77.0; bromophenols, 32.5; and chlorophenols, 8.3. With the stepwise decrease in recovery there is generally an increase in the melting and boiling points (Table II). Also, there is a tendency for the para isomer to be more soluble than the ortho and meta isomers (Table II). Isomeric phenolic compounds whose ortho isomer does not exhibit intramolecular hydrogen bonding to not behave in the above fashion. For example, 2-, 3-, and 4-methylphenol all give about 100% recovery in the steam distillation and their solubility in water (at ambient temperature) is about 2 g per 100 mL. Their melting points are 30.9, 11.5, and 34.8 °C, respectively, while their boiling points are 191, 202.2, and 201.9 °C, respectively. As can be seen from the results for λ_{max} and mε in Table I, intramolecular hydrogen bonding produces no particular trend insofar as the location of the peaks and their intensity is concerned.

Intramolecular hydrogen bonding has an important bearing on the recoveries for the di- and trihalogen phenols. It is known that such bonding occurs at the ortho position or positions, even when there are two or more substituents in

Table II. Melting Points, Boiling Points, and Solubilities of Phenolic Compounds Whose Ortho Isomers Exibit Intramolecular Hydrogen Bonding

compound	mp, °C	bp at 760 mm, °C	solubility (at room temp)[a]
2-nitrophenol	45–46	216	0.2 g/100 mL
3-nitrophenol	97	194 (at 70 mm)	1.4 g/100 mL
4-nitrophenol	114–116	279[b]	1.7 g/100 mL
2-methoxyphenol	32	205	slightly soluble
3-methoxyphenol	<−17	244.3	slightly soluble
4-methoxyphenol	57	243	soluble
2-bromophenol	5.6	194–195	slightly soluble
3-bromophenol	33	236.5	slightly soluble
4-bromophenol	66.4	238	soluble
2-chlorophenol	9.0	174.9	slightly soluble
3-chlorophenol	33	214	slightly soluble
4-chlorophenol	43–44	219.7	slightly soluble

[a] The solubilities of the nitrophenols are those given in ref 4. The solubility data for the methoxy-, bromo-, and chlorophenols given in the literature are questionable; hence the compounds are here characterized as being soluble or slightly soluble as is recommended in the last few editions of the "Handbook of Chemistry and Physics". [b] Decomposes and sublimes.

the ring (*6*, *7*). In the case of 2,3-dichlorophenol, 2,4-dichlorophenol, 2,4-dibromophenol, 2,4,5-trichlorophenol, and 2,4,6-trichlorophenol (two ortho positons), the intramolecular hydrogen at the ortho position or positions apparently overcomes the effect of the intermolecular hydrogen bonding at the other positions and almost complete recovery is obtained in the steam distillation. It is very significant that 3,5-dichlorophenol, which cannot undergo intramolecular hydrogen bonding, gives a low recovery (64.1%). All the di- and trihalogen phenols tested are considered to be slightly soluble in water. None precipitated on dilution of the 2-mL aliquot with water (producing for the spectral readings about an 0.004% solution).

The low volatility of the di- and trihydroxybenzenes in the steam distillation is readily explained by the very strong intermolecular hydrogen bonding of these compounds because of the multiple hydroxyl groups. The solubilities of the compounds (g per 100 mL) are as follows: pyrocatechol, 45; resorcinol, 147; hydroquinone, 6; pyrogallol, 51; and phloroglucinol, 1.1. The recovery of phenol, with the one hydroxyl group, was not quite complete (95.3%). The solubility of phenol is 9 g per 100 mL.

The NH_2 group can act as a donor or acceptor group in hydrogen bonding (*6*, *7*); consequently hydrogen bonding certainly occurs and can explain the low recoveries with the aminophenols. However, aminophenols are unique in that they are bases as well as acids and the amine salts formed in the acidic solution would not be expected to be volatile. The aminophenols are moderately soluble in water.

As the hydrocarbon portion of an alcohol or phenolic compound containing one hydroxyl group (and no other substituent groups) increases in size, the van der Waals forces between the moecules increase and consequently the effectiveness of the hydrogen bonding formation decreases (*8*). This decrease in hydrogen bonding could explain to some extent the very high recoveries for the monomethylphenols. It would certainly seem to explain the very high recoveries for the dimethylphenols, 4-*tert*-butylphenol, 4-*tert*-amylphenol, thymol, and carvacrol. It is known that in a long chain hydrocarbon the van der Waals forces are about 1.0 kcal per CH_2 unit. The dimethylphenols, 4-*tert*-butylphenol, 4-*tert*-amylphenol, thymol, and carvacrol are slightly soluble in water.

The low recoveries for 2,4-dinitrophenol (21.2%) and 2,4,6-trinitrophenol (0.0%) are due to polarizability effects, since two or more nitro groups in a phenol markedly increase the stability of phenolate ion by delocalizing the charge. A dinitrophenolate with its nitro groups in ortho and para positions allows delocalization of charge among three oxygens, while a trinitrophenolate with two ortho and one para group allows delocalization among four oxygens (*9*). The stability of the dinitrophenolate and trinitrophenolate ions manifests itself also in the very high acidity of the compounds. The pK_a of dinitrophenol is 3.96 and pK_a of 2,4,6-trinitrophenol is 0.38. There is no simple relationship between polarizability, pK_a, and hydrogen bonding (*6*, *7*).

Registry No. Phenol, 108-95-2; 2-nitrophenol, 88-75-5; 3-nitrophenol, 554-84-7; 4-nitrophenol, 100-02-7; 2-methoxyphenol, 90-05-1; 3-methoxyphenol, 150-19-6; 4-methoxyphenol, 150-76-5; 2-bromophenol, 95-56-7; 3-bromophenol, 591-20-8; 4-bromophenol, 106-41-2; 2-chlorophenol, 95-57-8; 3-chlorophenol, 108-43-0; 4-chlorophenol, 106-48-9; 2-methylphenol, 95-48-7; 3-methylphenol, 108-39-4; 4-methylphenol, 106-44-5; 4-chloro-2-methylphenol, 1570-64-5; 2,4-dimethylphenol, 105-67-9; 2,5-dimethylphenol, 95-87-4; 2,6-dimethylphenol, 576-26-1; 3,4-dimethylphenol, 95-65-8; 3,5-dimethylphenol, 108-68-9; 4-*tert*-butylphenol, 98-54-4; 4-*tert*-amylphenol, 80-46-6; thymol, 89-83-8; carvacrol, 499-75-2; 2,3-dichlorophenol, 576-24-9; 2,4-dichlorophenol, 120-83-2; 3,4-dichlorophenol, 95-77-2; 2,4,5-trichlorophenol, 95-95-4; 2,4,6-trichlorophenol, 88-06-2; 2,4-dibromophenol, 615-58-7; 2,4-dinitrophenol, 51-28-5; 2,4,6-trinitrophenol, 88-89-1; 2-aminophenol, 95-55-6; 3-aminophenol, 591-27-5; 4-aminophenol, 123-30-8; pyrocatechol, 120-80-9; resorcinol, 108-46-3; hydroquinone, 123-31-9; pyrogallol, 87-66-1; phloroglucinol, 108-73-6.

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