[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY'S MULTIPLE FELLOWSHIP AT MELLON INSTITUTE]

THE INFLUENCE OF LOCATION OF SUBSTITUENT GROUPS ON THE VAPOR PRESSURE OF ALKYLATED PHENOLS

ROBERT S. BOWMAN AND DONALD R. STEVENS

Received April 24, 1950

During the preparation of a long series of *tert*-butylated phenols there were a few instances in which some uncertainty arose as to the exact position taken by the entering *tert*-butyl group. A certain degree of clarification was obtained by studying the correlation between the position occupied by an alkyl group on the phenol nucleus and the attendant effect on the vapor pressure of the alklyphenol; this effect appears to be associated with the degree of intermolecular interaction, known as hydrogen bonding. While the results of the correlations cannot provide final, irrefutable evidence, they do offer strong support for the assignment of structure.

Upon the addition of an alkyl group to a phenol, one always observes a rise in boiling point (or lowering of vapor pressure) because of the increase in molecular weight. It is evident, however, that without exception the boiling-point increase attending *ortho*-alkylation is significantly smaller than that associated with *meta*- or *para*-alkylation (see Table I). Hence an *ortho*-alkylated phenol characteristically boils at a lower temperature than its *meta* or *para* isomer. Furthermore, whereas the boiling-point differences between the *ortho* and *meta*, or ortho and *para*, isomers are quite large, there invariably is only a small difference, if any, in boiling point between the *meta* and *para* isomers. The introduction of an alkyl group in a *meta* or *para* position on the phenol nucleus effectively lowers the vapor pressure to a much greater extent than does the addition of the same alkyl group when *ortho* to the hydroxyl group, apparently because of the attenuated degree of hydrogen bonding in the *ortho*-alkylphenols.

That hydrogen bonding is intimately associated with the relatively high boiling points of phenols can be demonstrated by the observation that the non-hydrogen-bonding alkylphenyl ethers boil at considerably lower temperatures than their corresponding hydrogen-bonding isomeric alkylphenols. Examination of the Hirschfelder atom models of the various alkylphenols shows, however, than an *ortho*-alkyl group can partially hinder the formation of intermolecular hydrogen bonds by virtue of its close proximity to the hydroxyl group. Since this partial screening effect cannot occur in the *meta*- and *para*-alkylated phenols, these isomers undergo more complete hydrogen bonding with resultant relatively lower vapor pressures or higher boiling points. Hence the extent of intermolecular hydrogen bonding influences the vapor pressure of a compound, and one is therefore able to predict the order of boiling points within a given series of alkylphenols.

The infrared absorption studies of Coggeshall (1) have verified the postulation of hindered hydrogen bonding. He found that the hindering capacity of a given *ortho*-alkyl group is related to its size and bulk, and that complete interference is manifested in an *o,o'*-dialkylphenol such as 2,6-di-*tert*-butyl-4-methylphenol where no intermolecular hydrogen bonds could be detected. The anticipated corollary, based upon vapor pressure effects, can be observed in Table III where the boiling-point differences between a series of *ortho*- and *para*-alkylated phenols can be seen to increase generally with the size and bulk of the alkyl group.

The series of *tert*-butylated phenols prepared and their boiling-point data are listed in Table II. All these compounds, except 2-*tert*-butylphenol and 3-methyl-4-*tert*-butylphenol, were synthesized by alkylating the starting phenol with isobutylene at atmospheric pressure and 70°, using five per cent by weight of concentrated sulfuric acid as the catalyst. In no instance was there any evidence for *meta*-alkylation or for the insertion of a *tert*-butyl group between two methyl groups, or between a methyl and a hydroxyl group placed *meta* to each other. For example, 3,5-dimethylphenol could not be butylated under these comparatively mild conditions, presumably because the active *ortho* and *para* positions are sufficiently hindered by the neighboring groups. Again, it is significant to note the complete conformity with the observation that *para* substitution is attended by the greater rise in boiling point. Also, the increases in boiling point become generally smaller as the number of alkyl groups on the parent phenol is increased. Figure 1 illustrates a characteristic division of the phenols into two broad groups; this is based on the graphing of the boiling-point increases accompanying *ortho*- and *para*-butylation. It is also apparent that the largest boiling-point increases occur when a 3- or 5-alkylphenol is butylated in the 4-position.

TABLE I

ALKYLATION *vs* BOILING-POINT INCREASE IN PHENOLS

NATURE OF ALKYL GROUP ADDED TO	BOILING POINT, °C./20 MM. AT POSITION			ATTENDANT INCREASE IN BOILING POINT, °C. AT POSITION		
	2	3	4	2	3	4
Phenol (85.0°)						
Methyl[b]	90.0	101.0	101.0	5.0	16.0	16.0
Ethyl[b]	101.5	114.5	115.0	16.0	29.5	30.0
n-Propyl[b]	122.0	127.0	128.0	37.0	42.0	43.0
Isopropyl[a]	106.0	120.0	120.0	27.0	35.0	38.0
n-Butyl[a]	123.0	138.0	138.0	38.0	53.0	53.0
sec-Butyl[a]	118.0	131.5	132.5	33.0	46.5	47.5
Isobutyl[a]	116.5	129.5	131.0	31.5	44.5	46.0
tert-Butyl[a]	113.0	129.5	130.0	28.0	44.5	45.0

[a] Data obtained in authors' laboratory.

[b] Pardee and Weinrich, *Ind. Eng. Chem.*, **36**, 595 (1944).

The observed "*ortho* effect" has been utilized in assigning the position taken by an entering *tert*-butyl group. For example, in the monobutylation of *o*-cresol, *m*-cresol, *o*-ethylphenol, *m*-ethylphenol, 2,3-dimethylphenol, and 2-*tert*-butyphenol, two isomers are formed in each instance. By noting and comparing the attendant boiling-point increases, the structures of the various products can be deduced

TABLE II

BOILING POINTS OF *tert*-BUTYLATED PHENOLS

ADDITION OF ONE *tert*-BUTYL GROUP TO	BOILING POINT, °C./20 MM.* POSITION OF ENTERING GROUP		ATTENDANT INCREASE IN BOILING POINT, °C./20 MM. POSITION OF ENTERING GROUP	
	2— or 6—	4—	2— or 6—	4—
Phenol (85°/20 mm.)	113.0	130.5	28.0	45.5
o-Cresol (90.0°/20 mm.)	118.0	132.0	28.0	42.0
m-Cresol (101.0°/20 mm.)	129.5	153.0	28.5	52.0
p-Cresol (101.0°/20 mm.)	126.0		25.0	
o-Ethylphenol (101.5°/20 mm.)	129.0	141.0	27.5	39.5
m-Ethylphenol (114.5°/20 mm.)	142.0		27.5	
p-Ethylphenol (115.0°/20 mm.)	137.0		25.0	
2,4-Dimethylphenol (105.0°/20 mm.)	131.0		25.0	
2,5-Dimethylphenol (105.0°/20 mm.)		151.0		46.0
2,6-Dimethylphenol (107.0°/20 mm.)		135.0	28.0	
2,3-Dimethylphenol (112.0°/20 mm.)	139.0	145.0	27.0	33.0
3,4-Dimethylphenol (122.0°/20 mm.)	143.0		21.0	
2-*tert*-Butylphenol (113.0°/20 mm.)		146.0		33.0
4-*tert*-Butylphenol (130.0°/20 mm.)	146.0		16.0	
2-Methyl-6-*tert*-butylphenol (118.0°/20 mm.)		149.0		31.0
2-Methyl-4-*tert*-butylphenol (132.0°/20 mm.)	149.0		17.0	
3-Methyl-6-*tert*-butylphenol (129.5°/20 mm.)		167.0		37.5
3-Methyl-4-*tert*-butylphenol (153.0°/20 mm.)	167.0		14.0	
4-Methyl-2-*tert*-butylphenol (126.0°/20 mm.)	147.0		21.0	
2,3-Dimethyl-6-*tert*-butylphenol (139.0°/20 mm.)		174.0		35.0
2,3-Dimethyl-4-*tert*-butylphenol	174.0		29.0	
2-Ethyl-6-*tert*-butylphenol (129.0°/20 mm.)		156.0		27.0
2-Ethyl-4-*tert*-butylphenol (141.0°/20 mm.)	156.0		15.0	
3-Ethyl-6-*tert*-butylphenol (142.0°/20 mm.)		174.0		32.0
4-Ethyl-2-*tert*-butylphenol (137.0°/20 mm.)	154.0		17.0	
2,4-Di-*tert*-butyphenol (146.0°/20 mm.)	158.0		12.0	

* Pardee and Weinrich, *Ind. Eng. Chem.*, **36**, 595 (1944).

TABLE III

BOILING-POINT DIFFERENCES IN *o*- AND *p*-ALKYLPHENOLS

ALKYLPHENOLS	DIFFERENCE IN B.P., °C. AT 20 MM.
o- and *p*-Methylphenols	11.0
o- and *p*-Ethylphenols	14.0
o- and *p*-Isopropylphenols	14.0
o- and *p*-*n*-Butylphenols	15.0
o- and *p*-*sec*-Butylphenols	14.5
o- and *p*-Isobutylphenols	14.5
o- and *p*-*tert*-Butylphenols	17.0

by analogy. Hence the *tert*-butyl-*o*-cresol (b.p. 118.0°/20 mm.) is 2-methyl-6-*tert*-butylphenol and the higher-boiling isomer (b.p. 132.0°/20 mm.) is the 2-methyl-4-

tert-butylphenol. These structures are further substantiated by the fact that the introduction of another *tert*-butyl group in 2-methyl-6-*tert*-butylphenol is accompanied by a greater increase in boiling point than is the introduction of a *tert*-butyl group in 2-methyl-4-*tert*-butylphenol; this is another indication that the 4-position is not occupied in the isomer assumed to be 2-methyl-6-*tert*-butylphenol.

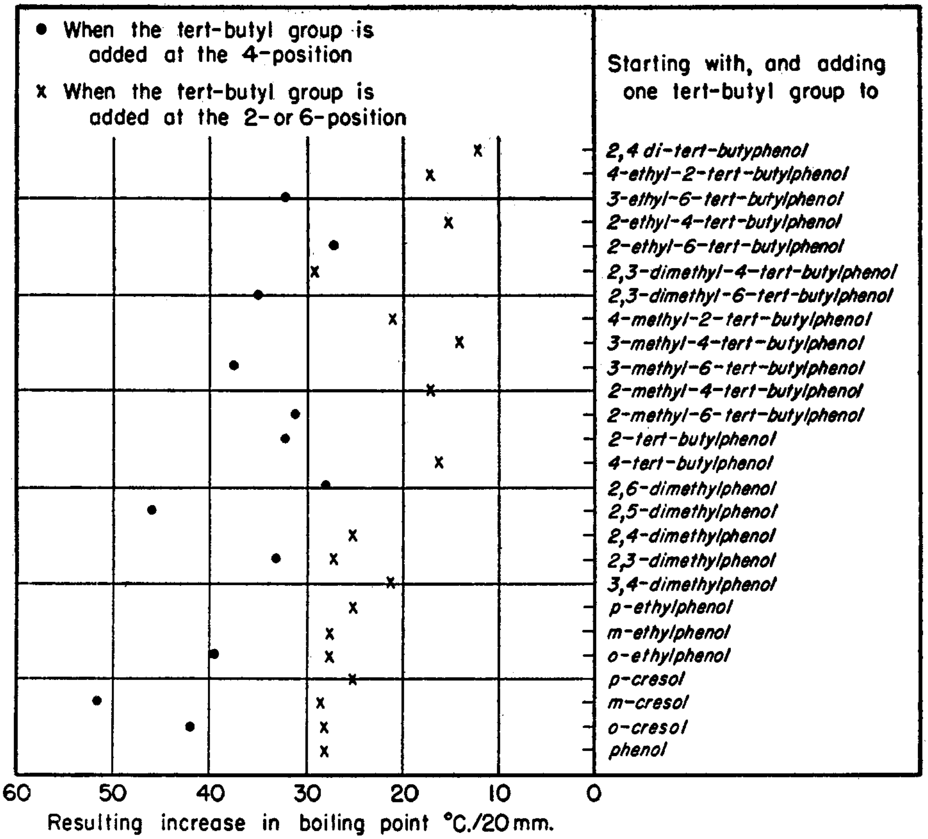

FIG. 1. Increase in boiling points attending substitution of *tert*-butyl groups in the 4-, and the 2- or 6-positions.

By the employment of similar reasoning, it is evident upon inspection of the data in Table II that the following designations can be made:

3-Methyl-*tert*-butylphenol (b.p. 129.5°/20 mm.) is 3-methyl-6-*tert*-butylphenol
3-Methyl-*tert*-butylphenol (b.p. 153.0°/29 mm.) is 3-methyl-4-*tert*-butylphenol
2-Ethyl-*tert*-butylphenol (b.p. 129.0°/20 mm.) is 2-ethyl-6-*tert*-butylphenol
2-Ethyl-*tert*-butylphenol (b.p. 141 0°/20 mm.) is 2-ethyl-4-*tert*-butylphenol
3-Ethyl-*tert*-butylphenol (b.p. 129.5°/20 mm.) is 3-ethyl-6-*tert*-butylphenol

(When the higher-boiling 3-ethyl-4-*tert*-butylphenol is prepared it probably will be found to boil in the neighborhood of 165°/20 mm.)

2,3-Dimethyl-*tert*-butylphenol (b.p. 139.0°/20 mm.) is 2,3-dimethyl-6-*tert*-butylphenol
2,3-Dimethyl-*tert*-butylphenol (b.p. 145.0°/20 mm.) is 2,3-dimethyl-4-*tert*-butylphenol
Di-*tert*-butylphenol (b.p. 146.0°/20 mm.) formed upon butylating 2-*tert*-butylphenol is 2,4-di-*tert*-butylphenol.

The assignment of a 6-position for the *tert*-butyl groups in both low-boiling *tert*-butyl-*o*-cresol and *tert*-butyl-*m*-cresol is also in accord with chemical evidence. Both of these isomers are less soluble in dilute alkali than their higher-boiling 4-*tert*-butyl isomers. Low alkali solubility is one of the characteristics of the hindered phenols, as shown by Stillson, Sawyer, and Hunt (2). In addition, the low-boiling 3-methyl-6-*tert*-butylphenol forms the urethan and phenoxyacetic acid derivatives at a noticeably slower rate than does the 3-methyl-4-*tert*-butylphenol, again indicating a steric hindrance effect attributable to the *ortho-tert*-butyl group in the 6-*tert*-butyl isomer.

SUMMARY

A general correlation, relating the effect of the location of an alkyl group upon the vapor pressure or boiling point of the alkylphenol, has been described. This correlation, explicable in terms of partial hindrance to intermolecular hydrogen bonding, affords support for the assignment of structures in certain *tert*-butylated phenols.

Pittsburgh, Pa.

REFERENCES

(1) Coggeshall, *J. Am. Chem. Soc.*, **69**, 1620 (1947).
(2) Stillson, Sawyer, and Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945).