The Correlation between the Relative Retention Behavior and the Number of Chlorine Substituents in the Phenol Ring

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Synopsis. The gas-chromatographic behavior of chlorinated phenols, *m*-cresols, and 3,5-xylenols on polar and nonpolar columns connected to either FID or ECD has been studied. The relative retention times (t_R) for individual homologous series were determined as a function of the number of chlorine substituents in the molecule. It was found, for the homologous series of these chlorinated compounds, that a relationship between log t_R and the number of chlorine substituents is of only limited use in the identification of individual chlorinated phenols.

Gas-liquid chromatography (GLC) is a rapid, specific, and sensitive method for the separation and determination of a variety of such volatile compounds as organic contaminants in the environment. The identification of the chromatographic separated components is, though, a complex problem, one which requires the use of many standards or a combination of gas chromatography and mass spectrometry (GC–MS). Some attempts to identify the compounds being chromatographed on the basis of their relative retention times (t_R) have been made, and it has been found that the plots of log t_R for many substituted phenols,[1] paraffins,[2] and organometalic compounds[3] against the number of carbon atoms in the molecule give straight lines. The corresponding relationships for organochlorine compounds have not yet been established, however.

Chlorination is extensively practiced in waste-water treatment in order to disinfect the effluent prior to discharge, particularly where the water may subsequently be used for recreational purposes or as a source of potable water. One class of compounds recognized as a major source of pollutants in the environment is the phenols. Phenols are introduced into the environment in several ways; directly as industrial effluents and indirectly as transformation products from natural and synthetic chemicals. It has now became evident that the treatment with chlorine of water which has been polluted with phenols leads to the formation of a variety of chlorinated phenols and quinones.[4] The aim of the present work is to reveal the relationships between the relative retention behavior of chlorinated phenols, *m*-cresols, and 3,5-xylenols and the number of chlorine substituents in the phenol ring, using both polar and nonpolar stationary phases. We then intend to use this relationship to identify the unknown samples in the environment.

Experimental

The chlorinated derivatives of phenol, *m*-cresol, and 3,5-xylenol used for the present work were obtained from various commercial sources; they are summarized in Table 1. These compounds were checked by GLC and mass spectrometry and were then used without further purification .

Table 1. Chlorinated phenols, *m*-cresols, and 3,5-xylenols examined in this investigation

Index number	Compound	Index number	Compound
1	Phenol	14	*m*-Cresol
2	2-Chlorophenol	15	4-Chloro-m-cresol
3	3-Chlorophenol	16	6-Chloro-m-cresol
4	4-Chlorophenol	17	4,6-Dichloro-m-cresol
5	2,3-Dichlorophenol	18	2,4,6-Trichloro-m-cresol
6	2,4-Dichlorophenol		
7	2,5-Dichlorophenol	19	3,5-Xylenol
8	2,6-Dichlorophenol	20	2-Chloro-3,5-xylenol
9	3,4-Dichlorophenol	21	4-Chloro-3,5-xylenol
10	2,4,5-Trichlorophenol	22	2,4-Dichloro-3,5-xylenol
11	2,4,6-Trichlorophenol		
12	2,3,4,6-Tetrachlorophenol	23	2,4,6-Trichloro-3,5-xylenol
13	2,3,4,5,6-Pentachlorophenol		

A Model 20-KE gas chromatograph (Japan Electron Optic Laboratory) equipped with an electron-capture detector (ECD, ^{63}Ni 10 mCi) and a Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector (FID) were used with nitrogen as the carrier gas. Two coiled glass tubes (2 m × 3 mm I. D), one packed with 10% Apiezon L/Chromosorb-W (AW-DMCS, 60—80 mesh) as the nonpolar stationary phase and the other packed with 5% DEGS+1% H_3PO_4/Chromosorb-W (AW-DMCS, 60—80 mesh) as the polar one, were used for the present work.

Results and Discussion

In the present work, both polar and nonpolar stationary phases, connected to either FID and ECD, were tested for the direct chromatography of chlorinated derivatives of phenol, *m*-cresol, and 3,5-xylenol. The t_R values for these compounds are presented graphically in Figs. 1 and 2 as a plot of log t_R against the number of chlorine substituents in the molecule. Although GLC's of several chlorinated phenols have been reported by earlier workers,[5] the present results appear to be the first detailed GLC data for these compounds.

Since it is known that plots of log t_R for many organic compounds against their boiling points give approximately straight lines,[6] the t_R values of compounds with lower numbers of chlorine substituents and with low boiling points may be expected to be smaller that those of compounds with higher numbers and high boiling points when the compounds are chromatographed on a nonpolar column. Figures 1 and 2 show that plots of log t_R against the number of chlorine substituents in the molecule give approximately straight lines for each homologous series of these chlorinated phenols, *m*-cresols, and 3,5-xylenols, with few exceptions.

Figures 1 and 2 also show that the smallest t_R values are found for compounds with chlorine atoms, at least

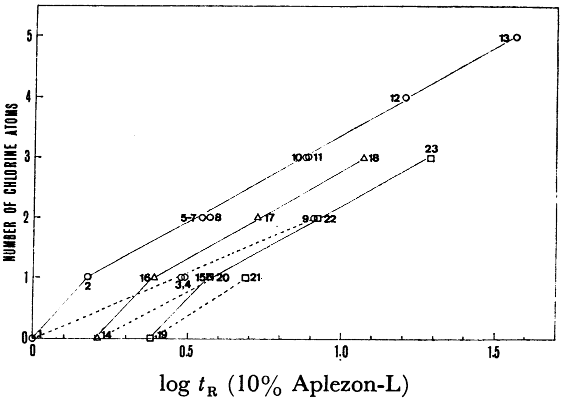

Fig. 1. Plot of log t_R against number of chlorine substituents in the molecule, using nonpolar column at 200 °C and 50 ml/min of N_2 as the carrier gas.
Chlorinated phenols; ○, chlorinated *m*-cresols; △, chlorinated 3,5-xylenols, □. Compound numbers, as in Table 1.

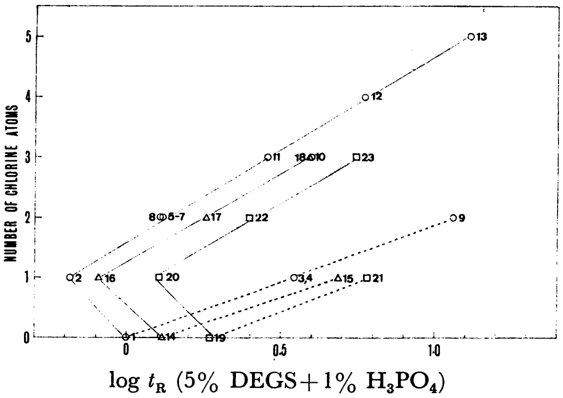

Fig. 2. Plot of log t_R against number of chlorine substituents in the molecule, using polar column at 160 °C and 50 mlmin of N_2 as the carrier gas.
Chlorinated phenols; ○, chlorinated *m*-cresols; △, chlorinated 3,5-xylenols; □. Compound numers, as in Table 1.

one of which is substituted on the ortho-position in the phenol ring (Solid lines) in comparison with those of the meta- and/or para-chlorinated isomers (dashed lines). In addition, these compounds (Points 3, 4, 9, 15, and 21) are characterized by larger t_R values on the polar column than those of the corresponding compounds with higher numbers of chlorine substituents. These results can be explained in terms of the steric shielding of the hydroxyl groups in phenols by chlorine atoms substituted on the ortho-position in the phenol ring, which prevents the formation of a hydrogen bond between the polar stationary phase and the chlorinated compounds.

Unfortunately, poor separations of *m*-chlorophenol from the para-isomer and of 2,3- from 2,4- and 2,5-dichlorophenol on both polar and nonpolar columns were observed, for these compounds have similar polarities and boiling points. In addition, the peaks of some compounds (*e.g.*, 2,6-dichlorophenol and 2-chloro-3,5-xylenol) overlapped when a mixture of these compounds was chromatographed on both polar and nonpolar columns. However, dichlorinated compounds among a mixture of mono- and dichloro-derivatives with similar t_R values on the columns could be assigned on the basis of the differences in ECD responses, because well-defined ECD peaks are observed for the ng order of a sample injected in the column connected to ECD, though these were very small ECD peaks for monochlorinated compounds in spite of the μg order of sample injection.

The response data indicated that the sensitiveties of FID for the chlorinated phenols became smaller with an increase in the number of chlorine substituents in the molecule, while those of ECD became larger. Similar relative ECD responses have been reported previously⁷⁾ for other aromatic halogeno and nitro compounds. These results can be explained in terms of the reduction of the flame-ionization current with organochlorine compounds, or as an increase in the electron-capture reactions with these compounds, which were, chromatographed on the column and then introduced into the detector.⁸⁾

The apparent differences in the FID and ECD sensitivities for the chlorinated derivatives of phenol, *m*-cresol, and 3,5-xylenol chromatographed on both polar and nonpolar columns may also arise as a result of peak broadening or narrowing associated with increases or decreases in t_R.

These results suggest that both the plots of log t_R against the number of chlorine substituents and the differences in ECD responses for the subject compounds can be used to investigate the chemical structure of chlorinated aromatic compounds formed during the chlorination of a variety of phenol compounds with aqueous hypochlorite.

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