distributions were given by the solid curves. In each case, it is found that the estimated distribution conforms quite closely to the central portion of the true distribution and is not strongly biased toward either of the tails. Thus, it appears that the estimation procedure described in this paper can reasonably be applied to real systems which may not necessarily conform to the log normal size distribution. The resulting, estimated distribution will be a kind of "best-fit" log normal approximation to the true particle size distribution.

## SUMMARY OF ESTIMATION PROCEDURE

The procedure to be followed in using this approach to estimate particle size distributions can be summarized as follows.

(1) Obtain the appropriate values of the light scattering coefficients  $K_t$  either from tables (see, for example, ref. 13 and 14) or by numerical solution of Equation 9.

(2) Determine the theoretical turbidity curves for the material by numerical integration of Equation 7.

(3) Measure the specific turbidity of the suspension as a function of solids concentration and extrapolate to infinite dilution. Obtain such measurements for at least two wavelengths.

(4) From the measured turbidities and the theoretical curves obtained in (2) above, determine the possible values of the mean size parameter  $\alpha_{50}$  corresponding to each value of the standard deviation  $\sigma$ .

(5) Plot  $\sigma$  vs. mean particle radius for each measured turbidity.

(6) Read off the estimated mean and standard deviation for the actual distribution from the intersection of the curves.

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# Chemically Bonded Aryl Ether Phase for the High Performance Liquid Chromatographic Separation of Aromatic Nitro Compounds

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A chemically bonded aryl ether stationary phase which shows novel selectivity in the reverse-phase liquid chromatographic separation of aromatic nitro compounds has been prepared. Differentiation between nitroaromatic isomers is a result of partitioning and charge transfer interactions. Comparisons with octadecyl and phenyl silica show both the differences and the advantages of the aryl ether phase. A modified Hammett equation is used to relate retention to electrophilic aromatic substitution rates for meta- and para-substituted compounds. Absorption spectra of the charge transfer complexes involved are presented, and the significance of the complexation is discussed in terms of its effect on chromatographic behavior.

Selectivity in high performance liquid chromatographic separations is often influenced by the electron donor-acceptor properties of the solute molecules and the bonded phase. While investigating the reverse-phase separation of a number

of aromatic nitro compounds, we hoped to take advantage of the strong electron accepting properties of these compounds by using a stationary phase which contained strong electron donating groups. The resultant charge transfer complexes are well documented in the literature (1-3), and it is basically accepted that there is a partial or complete transfer of electrons from donor to acceptor. Complex stability is a function of the electronic character and number of substituents on the acceptor molecule, their steric effects, and the solvent system employed. The interaction is highly suited for chromatographic application. Complexation kinetics are rapid (4), reversible, and discriminative enough to add functional group selectivity that is not possible in adsorption and partition chromatography.

The electron donor of choice for a nitroaromatic selective stationary phase is an aromatic ether. The ether linkage increases the electron density of the aromatic ring. The result is that the phenoxy group is one of the most powerful electron donors for nitroaromatics (1) as evidenced by formation of solid picrates. An organohalosilane incorporating the phenoxy group can be synthesized by the platinum catalyzed addition of a silicon hydride to an olefin (5, 6). The result is a terminally substituted silanizing reagent which may be chemically bonded to a silaceous chromatographic support material.

# EXPERIMENTAL

Chlorodimethyl-(3-phenoxy)propylsilane Synthesis. The platinum catalyzed addition of chlorodimethylsilane to allyl phenyl ether,



was run as follows: 7 g of allyl phenyl ether (0.0522 mol, 96% from Aldrich Chemical Corp., Inc.) and approximately  $1.0 \times 10^{-5}$ mol of chloroplatinic acid (Fisher Chemical) were heated to 85 °C with stirring in a 100-mL round bottom flask equipped with an efficient reflux condenser and dropping funnel. Five grams (0.05742 mol) of chlorodimethylsilane (Ventron Corp.) were added dropwise with stirring so that the heat of the reaction maintained the temperature between 90-100 °C. Total addition time was approximately 45 min. The solution was heated for an additional 8 h, the product vacuum distilled, and the fraction boiling between 90-92 °C at 0.25 mm Hg collected. The yield was 82% chlorodimethyl-(3-phenoxy)propylsilane. The 60-MHz proton magnetic resonance spectrum showed a 6-proton singlet at 0.40 ppm, a distorted 2-proton triplet at 0.90 ppm, 2-proton multiplet from 1.62 to 2.11 ppm, 2-proton triplet at 3.86 ppm, 3-proton multiplet at 6.89 ppm, and a 2-proton multiplet at 7.20 ppm. Aromatic resonances showed no significant differences from the starting material. A 70-eV mass spectrum gave results consistent with the position of addition and also with the absence of dimer resulting from hydrolysis.

Bonded Phase Preparation. Five grams of LiChrosorb SI60 5  $\mu$ m silica (E. M. Merck) were refluxed in 100 mL of 6 N hydrochloric acid for 2 h, filtered, washed thoroughly with neutral, distilled, deionized water, and dried under vacuum at 150 °C for 15 h. The above prepared silica and 50 mL of dry toluene were placed in a 250-mL round bottom flask equipped with an efficient reflux condenser. Three milliliters of chlorodimethyl-(3-phenoxy)propylsilane in 25 mL of dry toluene were added, and the whole was refluxed for 2 h. The bonded phase was filtered, washed thoroughly with dry toluene and methanol, and dried at 60 °C under vacuum for 15 h. Elemental carbon and hydrogen analysis showed percent loading to be 12.51% by weight, corresponding to 0.76 mmol of aryl ether per gram of support. This dry phase was suspended in 50 mL of dry toluene and treated with 4 mL of trimethylchlorosilane, refluxed for 1 h, filtered, washed with dry toluene and methanol, and dried under vacuum at 60 °C before use.

**Column Packing Procedure.** Stainless steel columns, 4 mm by 200 mm, were equipped with zero dead volume fittings. The packing (1.65 g) was slurried in 12 mL of isopropanol, sonicated for 30 s, and introduced into the column and packing reservoir. Filtered, distilled, deionized water, (200 mL) were pumped through at 6000 psi, and the column was conditioned with the appropriate mobile phase under normal operating conditions before use. Octadecyl and phenyl phases used in comparison studies were packed similarly.

**Chromatography.** The chemically bonded phenyl column used in comparison studies was prepared by treating  $5-\mu m$  Li-Chrosorb SI60 with dichloromethylphenylsilane. The  $5-\mu m$ octadecyl phase (ODS) was obtained from Johns-Manville. Column efficiencies were matched to range between 3000-3500 plates per 100 mm for comparison of the three columns. All flow rates were 1.00 mL/min. Mobile phases used for comparison studies were 50/50, 35/65, 6/94 methanol-water (v/v) for the aryl ether, ODS, and phenyl columns, respectively.

Molecular Complex Formation Studies. Solutions of allyl phenyl ether, nitroaromatic, and the two together in a 1 to 1 molar ratio, were prepared in 50/50 (v/v) methanol-water, and their ultraviolet absorption spectra run vs. 50/50 methanol-water. All

references were prepared identically to samples, excluding the nitro compound under investigation, when examining absorption shifts and intensity changes near the visible region.

Reagents and Instrumentation. The structure of chlorodimethyl-(3-phenoxy)propylsilane was confirmed with a Varian A-60 nuclear magnetic resonance spectrometer and a Perkin-Elmer-Hitachi RMU 6L mass spectrometer. A Perkin-Elmer 202 UV-vis spectrophotometer and a Beckman IR10 infrared spectrophotometer were used in complex formation studies. Liquid chromatograms were run on a Laboratory Data Control Constametric IIG liquid chromatograph equipped with a Model 1202 Spectromonitor II variable wavelength UV detector. Samples were introduced through a  $10-\mu L$  high pressure Valco injection valve. Methanol was Fisher Spectranalyzed grade. Water was distilled, run through cation- and anion-exchange columns as well as activated charcoal. All solvents were filtered through  $0.45-\mu m$ membrane filters. Most nitro compounds were commercially obtained. Others were synthesized using standard procedures and their identities were confirmed spectroscopically. All sample compounds were either fractionally distilled or recrystallized from the appropriate solvents, and their purities were checked by melting and boiling points.

## **RESULTS AND DISCUSSION**

Synthesis of the monochlorosilane is more desirable than the di- or trichloro derivative for several reasons. Hydride addition of chlorodimethylsilane proceeds much more slowly than the di- and trichloro reactions, making the addition easier to control. The resulting product is considerably more volatile than the di and tri derivatives which makes it easier to purify by fractional distillation. In addition, the effects of monofunctional vs. di- and trifunctional reagents on chromatographic performance have been reviewed in the literature (7, 8), showing that the monochloro reagent is more desirable because of its homogeneous, single layer coverage of the support material. Synthesis via silicon hydride addition is favored in this instance over other synthetic methods because of its high yield and selectivity for the terminally substituted isomer.

Column efficiencies for the aryl ether averaged 3500 plates in 100 mm using the loop injector. Up to 5000 plates per 100 mm were obtained by direct injection onto the same column. Peak shouldering and rapid column deterioration reduced the usefulness of this technique, however. Results of chromatography on the aryl ether, octadecyl, and phenyl columns are given in Table I in terms of k' values. Several general trends are evident. The elution order for the aryl ether is nonnitro, mononitro, dinitro, trinitro, showing that increased retention corresponds to decreasing electron density. A similar trend is not evident with either ODS or phenyl columns. These columns tend to retain polynitro compounds less strongly than mono and nonnitro because of the high polarity of the nitro group. The result, as shown in Table I, is that polynitro compounds of one class (i.e., dinitrobenzenes) have k' values similar to mononitro compounds of a different class (i.e., nitroacetanilides and nitrobenzaldehydes for ODS and phenyl respectively). The chromatograms in Figures 1a and 1b show the aryl ether elution order more clearly for a random mixture of nitro compounds varying widely in nature of substituents and solubility in the mobile phase. Of this mixture of 23 test compounds, ODS gave 16 distinct peaks while the phenyl column showed only 13. The latter two columns gave poor separation of the mixture in both cases due to co-elution of polynitros with mononitros.

Comparison separations of the three phases are shown in Figures 2 and 3. Separations of nitrobenzenes in Figure 2 show that the elution order for ODS is the inverse of the aryl ether. The phenyl phase (Figure 2c) gives a separation similar to ODS except for the early elution of benzene. Elution orders tend to indicate that ODS and, suprisingly, phenyl show little or no selectivity for electron density of the solutes. Hy-



**Figure 1.** (a) Mixture of aromatic nitro compounds separated isocratically on 4 mm i.d.  $\times$  200 mm long chemically bonded aryl ether phase. Mobile phase, 45% MeOH/55% H<sub>2</sub>O. Flow rate, 1.00 mL/min. UV detection at 254 nm, 0.08 AUFS. (1) *o*-Nitrobenzenesulfonamide, 236 ng; (2) *p*-nitrobenzenesulfonamide, 194 ng; (3) *p*-nitrobenzamide, 240 ng; aniline, 660 ng; (4) acetanilide, 210 ng; (5) *p*-nitrobenzoniline, 376 ng; (6) *o*-nitroacetanilide, 236 ng; (1) *o*-nitroaniline, 376 ng; (8) benzene, 3580 ng; *o*-nitrobenzonitrile, 236 ng; (9) *p*-nitrobenzonitrile, 236 ng; (10) *p*-nitrobenzenes, 378 ng; (12) *p*-dinitrobenzene, 178 ng; (13) *m*-dinitrobenzene, 158 ng; (14) 2,4-dinitroaniline, 222 ng; (15) *m*-nitroanisole, 184 ng; 2,4-dinitroacetanilide, 258 ng; (16) *p*-nitroanisole, 172 ng; (17) 1,3,5-trinitrobenzene, 120 ng; (18) 2,4-dinitroanisole, 176 ng; (20) 3,5-dinitromethylbenzoate, 210 ng. (b) Same mixture as in (a) run with a linear gradient from 35% MeOH to 65% MeOH. Gradient time equals 20 min



**Figure 2.** Comparison separations of nitrobenzenes on (a) aryl ether, (b) ODS, (c) phenyl. UV detection at 254 nm, 0.08 AUFS. (1) Benzene, 1790 ng; (2) nitrobenzene, 189 ng; (3) *p*-dinitrobenzene, 89 ng; (4) *m*-dinitrobenzene, 79 ng; (5) 1,3,5-trinitrobenzene, 60 ng

drophobic interaction appears to primarily govern distribution between the mobile and stationary phases in these latter two cases. Figure 3a distinctly shows separation according to the number of nitro substituents for compounds of similar polarity and solubility, yet different substituent classes. ODS and phenyl phases (Figures 3b and 3c) lack this selectivity, resulting in ineffective separation. This particular separation is of some significance to organic synthesis. Direct nitration of acetanilide is a common route to the o-, p-, and 2,4-dinitroanilines since these isomers cannot be obtained from the



**Figure 3.** Comparison separations of nitroanilines and nitroacetanilides on (a) aryl ether, (b) ODS, (c) phenyl. UV detection at 254 nm, 0.08 AUFS. (1) Aniline, 165 ng; (2) acetanilide, 52 ng; (3) *p*-nitroaniline, 94 ng; (4) *o*-nitroacetanilide, 84 ng; (5) *o*-nitroaniline, 74 ng; (6) *p*-nitroacetanilide, 90 ng; (7) 2,4-dinitroaniline, 56 ng; (8) 2,4-dinitroacetanilide, 64 ng

direct nitration of aniline. Mixtures of all isomers are possible in the process, and all are readily separated by the aryl ether bonded phase.

## Table I. k' Values for Standard Compounds

compound	aryl ether	ODS	phenyl
nonnitro			
aniline phenol acetanilide benzaldehyde benzonitrile benzene anisole	1.17 1.19 1.49 2.38 2.76 2.98 3.91	$1.71 \\ 2.26 \\ 2.57 \\ 3.71 \\ 3.76 \\ 8.18 \\ 8.14$	2.09 2.40 0.06 2.69 2.62 1.28 5.27
mononitro			
o-nitrobenzenesulfonamide p-nitrobenzenesulfonamide p-nitrobenzamide p-nitrobenzamide p-nitrophenol <sup>a</sup> m-nitrophenol <sup>a</sup> o-nitrobenzaldehyde o-nitrobenzaldehyde o-nitrobenzaldehyde o-nitrobenzaldehyde o-nitrobenzonitrile p-nitrobenzonitrile p-nitrobenzonitrile p-nitrobenzene o-nitrobenzene o-nitrobenzene p-nitroanisole p-nitroanisole p-nitroanisole p-nitroanisole p-nitroanisole p-nitroanisole p-nitroanisole p-nitroanisole	$\begin{array}{c} 1.00\\ 1.24\\ 1.31\\ 1.98\\ 2.06\\ 2.19\\ 2.33\\ 2.67\\ 2.79\\ 2.86\\ 2.87\\ 2.91\\ 2.98\\ 3.22\\ 3.24\\ 3.76\\ 4.86\\ 5.76\\ 6.19\\ 7.47\\ 8.18\end{array}$	$\begin{array}{c} 0.93\\ 1.23\\ 1.76\\ 2.50\\ 2.57\\ 3.86\\ 4.29\\ 4.78\\ 3.39\\ 5.90\\ 3.53\\ 5.20\\ 4.78\\ 3.43\\ 3.53\\ 5.81\\ 6.95\\ 6.40\\ 11.79\\ 8.82\\ 14.14\\ 16.14 \end{array}$	$\begin{array}{c} 1.40\\ 0.90\\ 1.42\\ 2.11\\ 2.14\\ 1.24\\ 1.51\\ 1.25\\ 2.60\\ 2.43\\ 3.26\\ 3.12\\ 4.23\\ 4.55\\ 2.47\\ 4.24\\ 3.48\\ 2.39\\ 5.20\\ 5.11\\ 6.13\\ 5.06 \end{array}$
dinitro			
3,5-dinitrobenzamide 2,6-dinitrophenol <sup>a</sup> 2,5-dinitrophenol <sup>a</sup> 2,4-dinitrophenol <sup>a</sup> <i>p</i> -dinitrobenzene <i>m</i> -dinitrobenzene 2,4-dinitroaniline 2,4-dinitroacetanilide 2,4-dinitroanisole 3,5-dinitro methyl benzoate	$2.90 \\ 3.28 \\ 3.85 \\ 4.22 \\ 4.40 \\ 4.88 \\ 5.11 \\ 5.84 \\ 8.02 \\ 13.81$	$\begin{array}{r} 4.42\\ 4.13\\ 5.17\\ 4.78\\ 5.54\\ 4.58\\ 7.30\\ 5.84\\ 14.14\\ 11.79\end{array}$	$1.90 \\ 2.25 \\ 1.94 \\ 1.94 \\ 3.29 \\ 2.43 \\ 3.89 \\ 4.60 \\ 6.31 \\ 6.54 $
trinitro			
1,3,5-trinitrobenzene 2,4,6-trinitroaniline	6.94 9.60	$\begin{array}{c} 3.13\\ 5.64\end{array}$	$\begin{array}{c} 1.77\\ 3.27\end{array}$
<sup>a</sup> Mobile phase modified with	1% by vo	lume ac	etic acid

Results of complex formation studies show absorption spectra characteristic of weakly bound molecular complexes. Figure 4 shows that the complex absorption spectrum of allyl phenyl ether and 1,3,5-trinitrobenzene is roughly the sum of the reactants, with slight anomaly in the 250- to 300-nm region. A significant increase in intensity, measured as the total area under the absorption curve, is present in  $4.5 \times 10^{-6}$  M solutions (Figure 4a). Such increases are characteristic of complex formation (9). An absorption shift toward the visible region, also indicative of charge transfer interactions, is not immediately apparent. It has been shown, however, that molecular complexes of this type often show spectra which are no more than the sum of the reactants when observed in dilute solutions (10). Increasing the molar concentration (Figure 4b) results in a significant increase in the absorption intensity between 300 and 350 nm. At higher concentrations, the intensity increase can be observed visually as a change from pale to deep yellow. Examination of the molecular complex formed between allyl phenyl ether and 2,5-dinitrophenol



**Figure 4.** Ultraviolet absorption spectra of 1,3,5-trinitrobenzene-allyl phenyl ether molecular complex. (Ai)  $4.5 \times 10^{-6}$  M allyl phenyl ether; (Aii) 1:1 molecular complex,  $4.5 \times 10^{-6}$  M; (Aiii)  $4.5 \times 10^{-6}$  M 1,-3,5-trinitrobenzene. (Bi)  $1.9 \times 10^{-2}$  M 1,3,5-trinitrobenzene; (Bii) 1:1 complex with allyl phenyl ether at same molar concentration

showed a 10-nm shift toward the visible region as well as increased spectrum intensity. At higher concentrations, this effect was also observed visually.

No significant changes were found in the infrared spectra of products compared to reactants. It has been shown (11) that changes in infrared bands do not necessarily appear, especially in weakly bound, noncrystalline complexes.

These data indicate that the complexes are weakly formed, and that partitioning into the stationary phase should be as much a factor in retention as is charge transfer interaction. This is particularly true with mononitro compounds which are only moderately electron deficient.

There is evidence of a relationship between molecular complex formation and the rate of electrophilic aromatic substitution in donors and acceptors (1, 12). Therefore, it should be possible to plot a modified Hammett equation (13)which relates the nature of substituents in substituted nitrobenzenes to chromatographic retention on the aryl ether. Since complex formation studies show that partitioning effects are important to retention, they must be taken into account by an approximation which gives a k' factor as a measure of electron density or charge transfer alone. A first approximation is to ratio the k' values of the aryl ether with those for a phase such as ODS which separates by partitioning. Incorporating this adjustment into the original Hammett equation gives

$$\log \left[ A(k'_{\rm ae}/k'_{\rm ods}) \right] = \rho \Sigma \sigma$$

where  $\sigma$  is the Hammett substituent constant,  $\rho$  the reaction constant, and A equal to the ratio of  $k'_{ods}$  to  $k'_{ae}$  for nitrobenzene. The equation gives a measure of the effects of substituents in nitrobenzenes compared to nitrobenzene through normalization by constant A. The calculations give a linear free-energy relationship which holds for para- and meta-substituted compounds only. The additivity principle (14) extends the application to poly-substituted compounds.

A plot of Hammett substituent constants (15) vs. the ODS normalized capacity factors is shown in Figure 5.  $\sigma^+$  values were used for the nitrobenzaldehydes and *p*-nitromethylbenzoate because of the unavailability in the literature of Hammett constants. The approximation roughly gives a linear relationship as predicted by theory. The nitroanilines, *p*nitrophenol, and *p*-nitroanisole deviate markedly in a positive direction, corresponding to retention greater than predicted. An explanation may lie in additional retention mechanisms, typically hydrogen bonding between the nitroanilines and *p*-nitrophenol and the bonded phase either linkage. In ad-



Figure 5. Hammett function data for para- and meta-substituted nitrobenzenes

dition, Hammett constants may not be accurate choices for these compounds since resonance effects of the substituents are not taken into account. Modified Hammett constants (15) improve the linearity and include some of the deviating points in the line.

A linear relationship between  $\log k'$  values and percent methanol in the mobile phase was observed for methanol contents between 35 and 65%. Ten nitrobenzenes, nitroanilines, and nitroacetanilides were investigated. This behavior is typical of other reverse-phase systems (16). Higher methanol contents showed positive deviation, or retention greater than expected.

In conclusion, we have found that the microparticulate aryl ether phase provides selectivity for aromatic nitro compound isomers that is not present in other nonpolar reverse-phase systems. It provides rapid and efficient separation of a large cross section of compounds typically found in nitration reaction mixtures and high explosive preparations, many of which are presently difficult to isolate by other means because of similarities in polarity and partitioning behavior.

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