

PAPER CHROMATOGRAPHY AND CHEMICAL STRUCTURE

VIII. HYPERCONJUGATION

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(Received June 26th, 1962)

INTRODUCTION

In a preceding part¹, we discussed the chromatography of alkylated phenols and showed that these substances obeyed MARTIN's equation² if atomic ΔR_M parameters were used for calculation purposes. A variation in the value of $\Delta R_M(H)$ was observed, depending on the proximity of CH_2 and CH groups to the aromatic ring and it was suggested that this variation was a result of the loosening of C-H bonds brought about by the polarization of alkyl groups attached to an aromatic structure. The polarization was regarded as possibly being produced by two mechanisms, carbon-hydrogen hyperconjugation and carbon-carbon hyperconjugation (the latter, according to BERLINER AND BONDHUS³, being the origin of the inductive effect in alkylbenzenes). Although it did not seem possible clearly to distinguish these two mechanisms chromatographically, the study described here sheds some further light on the problem.

EXPERIMENTAL AND RESULTS

Sheets of Whatman No. 4 paper were impregnated with olive oil (5% v/v in light petroleum) and the phenols were chromatographed by the descending method, using

TABLE I
CHROMATOGRAPHY OF SUBSTITUTED PHENOLS IN A REVERSED PHASE SYSTEM
(OLIVE OIL/70% ETHANOL)

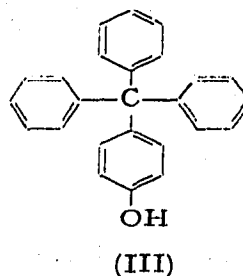
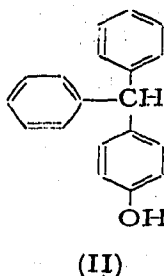
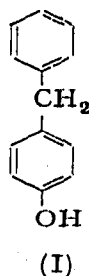
Compound	R_F	R_M	$\Delta R_M(\text{phenyl})$
Phenol		—1.142*	
<i>p</i> -Cresol		—1.008*	
<i>p</i> - <i>n</i> -Propylphenol	0.85	—0.740	
<i>p</i> - <i>n</i> -Butylphenol	0.80	—0.618	
<i>p</i> - <i>n</i> -Amylphenol	0.75	—0.483	
<i>p</i> -Phenylphenol	0.805	—0.620	+0.522
<i>p</i> -Benzylphenol (I)	0.805	—0.620	+0.388
<i>p</i> -Hydroxytriphenylmethane (II)	0.64	—0.250	+0.370
<i>p</i> -Hydroxytetraphenylmethane (III)	0.52	—0.036	+0.214

* Phenol and *p*-cresol both run rather too fast in this system for their R_M values to be found experimentally with the required degree of accuracy. They can be calculated with great precision, though, by extrapolation from the other homologous phenols, $\Delta R_M(CH_2)$ being +0.134 in this system.

70% (v/v) aqueous ethanol as mobile phase. After drying, the phenols were observed under ultra-violet light¹. Table I gives the R_F and R_M values of the compounds. As already described¹, R_M values were calculated directly and R_F values (to two significant figures) from them.

DISCUSSION

The three substances under investigation are phenyl-substituted phenols, as shown.



They can all be considered as derived from *p*-cresol by successive substitution of one α -hydrogen atom by a phenyl group.

$R_M(\text{phenyl})$ can be obtained by comparing R_M (*p*-phenylphenol) with $R_M(\text{phenol})$ and is equal to + 0.522. As *p*-phenylphenol and polynuclear phenols obey MARTIN'S equation with respect to atomic $\Delta R_M(\text{C})$ and $\Delta R_M(\text{H})$ parameters¹, this value for $\Delta R_M(\text{phenyl})$ can be considered as the additive increment for the phenyl group. (The loss of one hydrogen atom by the substitution in phenol to give *p*-phenylphenol can be considered as arbitrarily included in the parameter.) It is now possible to calculate the value of $\Delta R_M(\text{phenyl})$ obtained by adding successive phenyl groups to *p*-cresol. Table I shows that the value of this parameter is not constant, but decreases with increased substitution. The comparison between *p*-benzylphenol and cresol is, of course, an alternative expression of what we have previously referred to as the "allyl" effect and is produced by hyperconjugation of the benzyl group with the other aromatic ring. The fact that the value of $\Delta R_M(\text{phenyl})$ continues to decrease even in *p*-hydroxytetraphenylmethane (III), which contains no α -hydrogen atoms for carbon-hydrogen hyperconjugation, must mean that carbon-carbon hyperconjugation plays a predominant role in determining the nature of polarization in these molecules. A molecule such as (III) is approaching in structure certain compounds in which dissociation into stable free radicals occurs, and the aliphatic-aromatic carbon bonds in (III) must be subject to definite stretching. The relative decrease in $\Delta R_M(\text{phenyl})$ in these compounds—in (III) the whole phenyl group increases R_M by little more than one aliphatic CH_2 group—supports our previous suggestion¹ that hyperconjugation causes the deviations from MARTIN'S equation in alkylated and aryl-alkylated benzenes. It also supports the contention of BERLINER AND BONDHUS³ that carbon-carbon hyperconjugation may be more important than carbon-hydrogen conjugation in the ground state. Finally, it may be noted that there is no suggestion that the steric crowding in (II) or (III) produces any effect; if this existed it must produce an increase in R_M in a reversed phase system, that is, in the opposite direction to that found. This provides a further example of the apparent lack of importance of spatial effects compared to electronic effects in chromatography.

SUMMARY

The chromatography of a series of phenylated *p*-cresols has been studied. It provides evidence that carbon-carbon hyperconjugation is of importance in determining the R_M values of these compounds.

REFERENCES

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