

CHROM. 14,495

Note

Adsorption of chlorinated phenols on Sephadex LH-20

DAN JOHNELS*, ULF EDLUND and SVANTE WOLD

Department of Organic Chemistry, Institute of Chemistry, Umeå University, S-901 87 Umeå (Sweden)
and

CARL-AXEL NILSSON

National Board of Occupational Safety and Health, Department of Occupational Health, S-901 85 Umeå (Sweden)

(Received October 27th, 1981)

This study of the retention behaviour of chlorophenols was stimulated by our interest in multivariate structure–activity relationships of hazardous environmental compounds and a search for appropriate molecular descriptors in these studies.

Using Sephadex as adsorbent several investigations have been undertaken, eluting phenols and other aromatic compounds, in order to assess a valid retention mechanism. Determann and Walter suggested that the ether linkage between the dextran chains is the preferred site of adsorption¹. However, a complete understanding of the retention mechanism of these compounds on dextran gels is still lacking.

Brook and Housley, and later Brook and Munday, proposed that hydrogen bonding is the preferred mode of interaction, except for halogenated phenols, where the adsorption is governed by direct interaction between the halogen substituents and the dextran chains^{2,3}.

A contradictory proposal has been advanced by Streuli and Orloff, who claimed that phenols are adsorbed through π -bonding and hydrogen bonding⁴. De Ligny states that the adsorption of phenols is controlled not by hydrogen bonding, but by a phenol–dextran π -bonding⁵.

On several occasions deviating behaviour of chlorophenols has been noted³. However, so far only a limited number of chlorophenols have been studied. Therefore, in the present study we have included all possible isomers of chlorophenols and they were all studied on Sephadex LH-20, using chloroform as eluent.

MATERIALS AND METHODS

The chlorophenols were eluted through a 14.2 × 2.45 cm column packed with Sephadex LH-20, using chloroform as eluent. The flow-rate was 0.75 ml/min. A LKB 2089 UVICORD III was used as detector (275 nm). A 100- μ l volume of the chlorophenol was injected on to the column, and the concentration was 0.3 M except for pentachlorophenol where the concentration was 0.24 M owing to restricted solubility. The retention was characterized by the retention volume V_R . The reported V_R values are calculated means from three independent runs.

The chlorophenols were commercially available. The chloroform was obtained from May & Baker (Dagenham, Great Britain) and redistilled before use. Sephadex LH-20 (Batch No 2167) was purchased from Pharmacia (Uppsala, Sweden).

The IR measurements have been reported previously by Perelygin and Akhunov⁶. They used carbon tetrachloride as solvent and acetonitrile as hydrogen acceptor.

RESULTS AND DISCUSSION

V_R and IR data ($\Delta v/v$) are listed in Table I. The correlation between V_R and $\Delta v/v$ is further illustrated in Fig. 1.

TABLE I

RETENTION VOLUMES (V_R) AND PROTON-DONATING ABILITIES ($\Delta v/v$) OF THE CHLOROPHENOLS

Chlorine substitution	No.	V_R/ml	$\Delta v/v^*$
2,6	1	87	0.0594
2,4,6	2	113	0.0642
2,3,6	3	113	0.0651
2,3,4,6	4	137	0.0696
2,3,5,6	5	138	—
2,3,4,5,6	6	163	0.0752
2	7	122	0.0538
2,3	8	166	—
2,4	9	175	0.0589
2,5	10	196	0.0609
2,3,4	11	218	0.0647
2,3,5	12	257	—
2,4,5	13	266	0.0652
2,3,4,5	14	309	—
—	15	368	0.0463
4	16	494	0.0507
3	17	544	0.0533
3,4	18	652	0.0572
3,5	19	683	0.0603
3,4,5	20	757	0.0634

* Ref. 6.

A separation into three distinct classes is quite obvious and caused by the actual type of *ortho* substitution (an identical correlation was observed if we used the $\Delta\delta_{OH,dil}$ NMR differentials, as expected)⁷. A correlation with $\Delta v/v$ is observed in each class, *i.e.* increasing proton-donating ability of the phenol causes a larger V_R value. Any other physical interaction correlated with $\Delta v/v$ is of course possible, but we have chosen the proton-donating ability of the phenol.

If the retention was dominated by a π -bonding interaction, we would observe lower V_R values by increasing the degree of chlorine substitution, because the π -bonding ability is expected to decrease if electron-accepting substituents are intro-

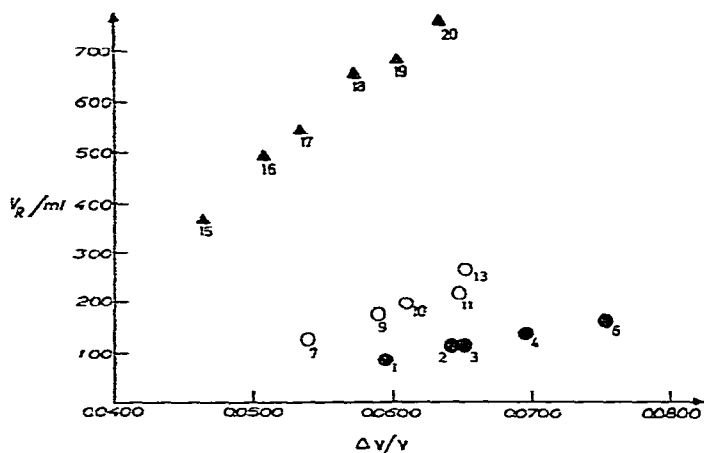


Fig. 1. Retention volume V_R as a function of the proton-donating ability $\Delta v/v$. \blacktriangle , no *ortho* chlorines; \circ , one *ortho* chlorine; \bullet , two *ortho* chlorines.

duced⁸. As is evident from Fig. 1 this is not the case. Thus π -bonding or variation in π -bonding is hardly important in our chromatographic system.

If we consider direct gel-substituent interactions, as earlier proposed³, this could possibly account for the behaviour in each class, but the dependence of *ortho* substitution would not be so dramatic.

However, the correlation between V_R and the proton-donating ability is not necessarily valid under other conditions. It has recently been observed⁹ that by changing the system to silica gel/dichloromethane-hexane (40:60) one obtains a reasonable correlation with a parameter inversely proportional to $\Delta v/v$. This observation supports Streuli's idea that several retention mechanisms can be operative for a given compound and the relative importance of each is determined by the actual experimental conditions¹⁰.

For the general case of substituted phenols at least two mechanisms exist, a proposal that is supported by the data of Haglund¹¹, but this conclusion is not reached in her work. If direct gel-substituent and/or gel- π interactions are excluded, the retention behaviour is closely correlated with the hydrogen-bonding ability¹¹.

REFERENCES

- 1 H. Determann and I. Walter, *Nature (London)*, 219 (1968) 604.
- 2 A. J. W. Brook and S. Housley, *J. Chromatogr.*, 41 (1969) 200.
- 3 A. J. W. Brook and K. C. Munday, *J. Chromatogr.*, 47 (1970) 1.
- 4 C. A. Streuli and M. Orloff, *J. Chromatogr.*, 62 (1971) 73.
- 5 C. L. De Ligny, *J. Chromatogr.*, 172 (1979) 397.
- 6 I. S. Perelygin and T. F. Akhunov, *Opt. Spectrosc.*, 30 (1971) 367.
- 7 D. P. Eyman and R. S. Drago, *J. Amer. Chem. Soc.*, 88 (1966) 1617.
- 8 I. S. Perelygin and T. F. Akhunov, *Opt. Spectrosc.*, 33 (1972) 132.
- 9 A. Bjørseth and K. Ugland Sogn, personal communication.
- 10 C. A. Streuli, *J. Chromatogr.*, 56 (1971) 225.
- 11 Å. Ch. Haglund, *J. Chromatogr.*, 156 (1978) 317.