Journal of Chromatography, 76 (1973) 185–189

CHROM. 6369

CHROMATOGRAPHIC BEHAVIOUR AND CHEMICAL STRUCTURE OF AROMATIC ALDOXIMES

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(First received April 27th, 1972; revised manuscript received September 24th, 1972)

SUMMARY

The R_M values of 15 pairs of isomeric (*syn* and *anti*) aromatic aldoximes investigated illustrate the validity of MARTIN's theoretical postulates for the relationship between chemical structure and R_F values in partition chromatography. Oximes were separated by thin-layer chromatography on Silica Gel G with the mobile phase benzene–ethyl acetate (5:1, v/v). The calculation of group constants and binding increments, for both *syn* and *anti* series, was carried out by direct comparison of the R_M values of substances that differed by only one group or increment. These data can facilitate the chromatographic elucidation of structural problems.

INTRODUCTION

The linear relationship between the R_M value[1] and the number of identical groups in partition chromatography, based on the predictions of CONSDEN *et al.*[2] and MARTIN[3], has been verified experimentally by various workers[4,5]:

$$R_M = G_0 + nG_x + mG_y \ldots \quad (1)$$

where G_0 is a basic constant and G_x, G_y, . . . are group constants of x, y, ...

Some of these group constants are known in paper chromatography[1,6,7], but for thin-layer chromatography (TLC), which is more suitable for the separation of oximes[8–10], only a few constants have been published[5,10–14]. Furthermore, in TLC, the contribution of one group to the R_M value of the molecule is dependent on the other groups in the molecule; this effect was shown by PATAKI[11], who compared the R_M values of amino acids that differed by specific groups.

The aim of this work was to establish group constants from the R_F values of aromatic aldoximes in the *syn* and *anti* series. In addition, the effect of criteria that have hardly been considered in the past, for instance binding increments, such as with double bonds, and the relative positions of substituents in the aromatic ring, were taken into account. The data obtained could be of use in the elucidation of structural problems.

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EXPERIMENTAL

The separation of oximes was carried out on Silica Gel G (Stahl) layers, with the mobile phase benzene–ethyl acetate (5 : 1, v/v), at 23°. Details regarding the preparation of the plates, the solvent system, the time of development, the detection reagent and the technique in general were given in a previous paper on the TLC of isomeric oximes[8].

To correlate the chromatographic behaviour of substances with their chemical structures, an accurate knowledge of the R_F values is necessary. We used conventional equipment but in order to obtain reproducible and accurate results we observed strictly the following points: constant temperature, time of saturation and size of spots.

RESULTS AND DISCUSSION

Two forms of each oxime are theoretically possible, *viz.*, *syn* and *anti*, and their separation by chromatography has been reported in only a few papers. ZECHMEISTER[15] made use of column adsorption chromatography, while PEJKOVIĆ-TADIĆ and co-workers[8–10] showed that TLC is a convenient and rapid method for the analytical separation and determination of isomeric oximes.

We focused our attention on the investigation of aromatic aldoximes by TLC. The experimental R_F and R_M values of aromatic aldoximes, as well as R_F and R_M values calculated by means of the established group constants, are given in Tables I and II. The differences in R_M values, *i.e.*, ΔR_M, are presented in the

TABLE I

R_F VALUES OF ISOMERIC AROMATIC ALDOXIMES

Adsorbent: Silica Gel G (Stahl). Mobile phase: benzene–ethyl acetate (5 : 1, v/v). Temperature: 23 ± 1°.

Oxime	$R_F \times 10^{8a}$	
	Syn	*Anti*
Benzaldoxime[b]	50.0	32.0
4-Methylbenzaldoxime[c]	54.3	33.5
4-Methoxybenzaldoxime[c]	42.8	27.1
4-Isopropylbenzaldoxime[c]	54.8	37.1
2-Nitrobenzaldoxime[c]	47.1	40.0
3-Nitrobenzaldoxime[c]	52.8	35.7
4-Nitrobenzaldoxime[c]	53.5	34.3
2-Chlorbenzaldoxime	53.5	45.7
3-Chlorbenzaldoxime	55.0	38.5
4-Chlorbenzaldoxime	55.7	37.8
Cinnamaldoxime (C=C *trans*)	59.6	50.0
2-Nitrocinnamaldoxime	55.7	57.8
3-Nitrocinnamaldoxime	62.1	53.5
4-Nitrocinnamaldoxime	64.3	51.4
4-Chlorcinnamaldoxime	64.9	55.7

[a] Mean value from at least 6 determinations.
[b] *Cf.* ref. 8.
[c] *Cf.* ref. 11.

final column of Table II. It can be seen that the agreement between the experimental and calculated R_M values is very satisfactory in the cases investigated, *i.e.*, the highest discrepancy in R_M is +0.025 in the *syn* series (4-nitrocinnamaldoxime) and −0.021 in the *anti* series (4-nitrocinnamaldoxime). It should be pointed out that the agreement is good even for 2-nitrocinnamaldoxime, which, unlike any of the other aldoximes investigated, has a lower R_F value for the *syn* than for the *anti* form. (This might possibly be explained by the vicinity of the 2-NO_2 group and the double bond in the side-chain.)

In the aliphatic series of aldoximes, it has previously been shown[10] that there is a linear relationship between the number of carbon atoms in the molecule and the R_M value. The difference in the R_M values between the successive members of the homologous series gave the constants for the $-CH_2$ group, $G_{(CH_2)}$, of −0.051

TABLE II

R_M VALUES OF ISOMERIC AROMATIC ALDOXIMES

Oxime	*Syn*			*Anti*		
	Found	*Calculated*	ΔR_M	*Found*	*Calculated*	ΔR_M
Benzaldoxime	+0.000	—	—	+0.327	—	—
4-Methylbenzaldoxime	−0.075	—	—	+0.298	—	—
4-Methoxybenzaldoxime	+0.126	—	—	+0.430	—	—
4-Isopropylbenzaldoxime	−0.084	—	—	+0.229	—	—
2-Nitrobenzaldoxime	+0.050	—	—	+0.176	—	—
3-Nitrobenzaldoxime	−0.049	—	—	+0.256	—	—
4-Nitrobenzaldoxime	−0.061	—	—	+0.282	—	—
2-Chlorbenzaldoxime	−0.061	—	—	+0.075	—	—
3-Chlorbenzaldoxime	−0.087	—	—	+0.203	—	—
4-Chlorbenzaldoxime	−0.100	—	—	+0.218	—	—
Cinnamaldoxime	−0.169	—	—	+0.000	—	—
2-Nitrocinnamaldoxime	−0.100	−0.122	−0.022	+0.136	−0.154	−0.018
3-Nitrocinnamaldoxime	−0.215	−0.220	−0.005	+0.061	−0.071	−0.010
4-Nitrocinnamaldoxime	−0.256	−0.231	+0.025	+0.024	−0.045	−0.021
4-Chlorcinnamaldoxime	−0.267	−0.271	−0.004	+0.100	−0.108	−0.008

TABLE III

GROUP CONSTANTS AND BINDING INCREMENTS

Adsorbent: Silica Gel G (Stahl). Mobile phase: benzene–ethyl acetate (5:1, v/v). Temperature: 23 ± 1°.

Group	*Syn*	*Anti*
CH=NOH	+0.130	+0.188
C_6H_5	−0.130	+0.139
CH=CH (*trans*)	−0.169	−0.327
CH_3 in position 4	−0.075	−0.029
OCH_3 in position 4	+0.126	+0.103
$CH(CH_3)_2$ in position 4	−0.084	−0.098
NO_2 in position 2	+0.050	−0.151
NO_2 in position 3	−0.049	−0.071
NO_2 in position 4	−0.061	−0.045
Cl in position 2	−0.061	−0.252
Cl in position 3	−0.087	−0.124
Cl in position 4	−0.100	−0.109

($\pm$0.015) in the *syn* series and $-$0.031 ($\pm$0.007) in the *anti* series. Taking this value as the starting point, the $G_{(CH=NOH)}$ value has been calculated from the data for the aliphatic series in the following manner:

$$G_{(CH=NOH),syn} = R_{M(heptaldoxime,syn)} - 6 \times G_{(CH_2),syn}$$
$$= -0.176 - 6 \times (-0.051)$$
$$= -0.176 - 0.306$$
$$= 0.130$$

$$G_{(CH=NOH),syn} = R_{M(hexaldoxime,syn)} - 5 \times G_{(CH_2),syn}$$
$$= -0.125 - 5 \times (-0.051)$$
$$= -0.125 - 0.255$$
$$= 0.130$$

$$G_{(CH=NOH),anti} = R_{M(propionaldoxime,anti)} - 2 \times G_{(CH_2),anti}$$
$$= 0.125 - 2 \times (-0.031)$$
$$= 0.125 - 0.062$$
$$= 0.187$$

$$G_{(CH=NOH),anti} = R_{M(butyraldoxime,anti)} - 3 \times G_{(CH_2),anti}$$
$$= 0.099 - 3 \times (-0.031)$$
$$= 0.099 - 0.093$$
$$= 0.192$$

The mean values from six aliphatic aldoximes are:

$$G_{(CH=NOH),syn} = 0.130\,(\pm 0.001)$$
$$G_{(CH=NOH),anti} = 0.188\,(\pm 0.003)$$

All the other group constants and binding increments, given in Table III, were calculated as the difference between the R_M values of two compounds that differed by only one group or increment in question. Thus:

$$G_{(2\text{-}NO_2),syn} = R_{M(2\text{-nitrobenzaldoxime},syn)} - R_{M(benzaldoxime,syn)}$$
$$= 0.050 - 0.000$$
$$= 0.050$$

$$G_{(2\text{-}NO_2),anti} = R_{M(2\text{-nitrobenzaldoxime},anti)} - R_{M(benzaldoxime,anti)}$$
$$= 0.176 - 0.327$$
$$= -0.151$$

$$G_{(CH=CH,trans),syn} = R_{M(cinnamaldoxime,trans,syn)} - R_{M(benzaldoxime,syn)}$$
$$= -0.165 - 0.000$$
$$= -0.165$$

$$G_{(CH=CH,trans),anti} = R_{M(cinnamaldoxime,trans,anti)} - R_{M(benzaldoxime,anti)}$$
$$= 0.000 - 0.327$$
$$= -0.327$$

Finally, it should be mentioned that for the calculation of group constants in this manner, *i.e.*, by the direct comparison of R_M values of substances that differ by only one group, the basic constant need not be known.

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