

CHROM. 7500

## THIN-LAYER CHROMATOGRAPHIC DETERMINATION OF THE STABILITY OF COMPLEXES OF SUBSTITUTED STYRENES ON SILVER NITRATE-IMPREGNATED SILICA

A. P. G. KIEBOOM, N. DE KRUYF and H. VAN BEKKUM

*Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, Delft-2208 (The Netherlands)*

(First received December 27th, 1973; revised manuscript received April 9th, 1974)

---

### SUMMARY

A quantitative approach is presented for the determination of complexing strengths by means of thin-layer chromatography. This approach has been applied to the silver (I) complexes of a series of 3- and 4-substituted styrenes. The results are considered in terms of a Hammett-Yukawa relationship with a  $\rho$  value of  $-0.8$ , which is close to the results obtained from solubility and distribution measurements.

---

### INTRODUCTION

Of the various methods for measuring the strength of interaction between a metal and a ligand, recently reviewed by Hartley<sup>1</sup> for complexes between unsaturated hydrocarbons and transition metals, the use of thin-layer<sup>2</sup> and column liquid chromatography<sup>3</sup> has received little attention. In particular, these chromatographic methods may offer a convenient and rapid means for the study of the stability of complexes between a metal ion or atom and a ligand in solution. Furthermore, liquid chromatography may be complementary to the well developed gas chromatographic method in the case of non-volatile ligands.

In this paper, we present a quantitative approach to the study of metal-ligand interactions by means of thin-layer chromatography (TLC). In order to test the method, we studied the silver(I) complexes of a series of 3- and 4-substituted styrenes on silver nitrate-impregnated silica. Comparison is made with literature results obtained from direct solubility and distribution measurements.

### EXPERIMENTAL

The styrenes were commercial samples or preparations made by standard procedures<sup>4,5</sup>. The pre-coated silica gel plates (20 × 20 cm) were purchased from Merck, Darmstadt, G.F.R., (Silicagel 60, layer thickness 0.25 mm). The silica area was 260 m<sup>2</sup>/g (nitrogen adsorption), pore volume 1.6 ml/g, mean pore radius 140 Å (mercury penetration), and water content 8%, after heating for 1 h at 120° (loss of weight after subsequent heating of the silica for 65 h at 400°).

The silver nitrate-impregnated silica gel plates were prepared by immersing the pre-coated plates in a solution of silver nitrate in acetonitrile for 30 min, followed by

drying for 60 min at 120°. The use of solutions containing 0.1, 3, 6, 10 and 20% (w/v) of silver nitrate yielded plates with a loading of 0.00, 0.025, 0.07, 0.15, 0.23 and 0.47 g of silver nitrate per gram of silica.

Samples (6  $\mu$ l) of a 1% solution of the styrenes in *n*-heptane were spotted on the plates, developed with chloroform at room temperature and rendered visible with phosphomolybdic acid<sup>6</sup> (20% solution in ethanol).

## THEORETICAL

Consider the complexation of a ligand L in solution with metal ions M impregnated on a support S under TLC conditions. The stationary phase consists of both M and S and the interactions of the ligand with the stationary phase have to be described in terms of both a complex constant  $K_M$  and an adsorption equilibrium constant  $K_S$ .

For the transfer of 1 mole of L from the stationary phase to the mobile phase, the reversible work due to complexation of L with M (denoted by  $W_{rev,M}$ ) is given by<sup>7</sup>

$$W_{rev,M} = RT \left( \ln \frac{C_m}{C_M} - \ln K_M \right) \quad (1)$$

where  $C_m$  and  $C_M$  are the amounts of the mobile phase and M, respectively\*. When  $n$  molecules of L are transferred from the stationary to the mobile phase, or when one molecule of L is transferred  $n$  times from the stationary to the mobile phase, the reversible work delivered is  $n/N \cdot W_{rev,M}$  ( $N$  = Avogadro constant). Comparison of a ligand  $L_0$  with some other ligand  $L_1$  under the same conditions leads to

$$\frac{n}{N} (W_{rev,M})_{L_1} - \frac{n}{N} (W_{rev,M})_{L_0} = -\frac{n}{N} RT \ln \frac{(K_M)_{L_1}}{(K_M)_{L_0}} = \frac{n}{N} [(\Delta G_M)_{L_1} - (\Delta G_M)_{L_0}] \quad (2)$$

where  $\Delta G_M$  is the free energy of complex formation between the ligand and M. The  $K_M$  values are given by<sup>7</sup>

$$K_M = \frac{C_m}{C_M} (1/R_F^M - 1) \quad (3)$$

where  $R_F^M$  denotes the  $R_F$  value of the ligand developed on an imaginary TLC plate with just M as the stationary phase and  $n=N$ . Combining eqns. 1 and 3 gives

$$W_{rev,M} = -RT \ln (1/R_F^M - 1) \quad (4)$$

However, the experimental  $R_F$  values are determined by both M and S complex formation. Furthermore, these  $R_F$  values count for  $n$  instead of  $N$  interactions between the ligand and M, *i.e.*, they refer to  $n/N \cdot W_{rev,M}$  rather than  $W_{rev,M}$ . The following expression can be written:

$$[(W_{rev,MS})_{L_1} - (W_{rev,MS})_{L_0}] - \theta [(W_{rev,S})_{L_1} - (W_{rev,S})_{L_0}] = \frac{n}{N} [(W_{rev,M})_{L_1} - (W_{rev,M})_{L_0}] \quad (5)$$

where  $W_{rev,MS}$  and  $W_{rev,S}$  are the reversible work pertaining to the M-impregnated

\* The ratio  $C_m/C_M$  may vary along the length of the chromatogram<sup>8</sup>. However, this phenomenon is eliminated later by the use of relative  $K$  values (*cf.*, eqns. 8, 10 and 12).

S and the S stationary phase, respectively, whereas  $1-\theta$  ( $0 \leq \theta \leq 1$ ) is the fraction of the surface area of S covered by M. By analogy with eqn. 4, we can write

$$(W_{\text{rev,MS}}) = -RT \ln (1/R_F^{\text{MS}} - 1) \quad (6)$$

and

$$(W_{\text{rev,S}}) = -RT \ln (1/R_F^{\text{S}} - 1) \quad (7)$$

where  $R_F^{\text{MS}}$  and  $R_F^{\text{S}}$  are the respective  $R_F$  values of the ligand on the plates. Substitution of eqns. 6 and 7 for  $L_0$  and  $L_1$  in eqns. 2 and 5 gives

$$\begin{aligned} \frac{n}{N} [(W_{\text{rev,M}})_{L_1} - (W_{\text{rev,M}})_{L_0}] &= RT \ln \left[ \frac{(1/R_F^{\text{MS}} - 1)_{L_1}}{(1/R_F^{\text{MS}} - 1)_{L_0}} \right] - \theta RT \ln \left[ \frac{(1/R_F^{\text{S}} - 1)_{L_1}}{(1/R_F^{\text{S}} - 1)_{L_0}} \right] \\ &= -\frac{n}{N} RT \ln \frac{(K_M)_{L_1}}{(K_M)_{L_0}} = \frac{n}{N} [(\Delta G_M)_{L_1} - (\Delta G_M)_{L_0}] \quad (8) \end{aligned}$$

In the case of structurally related ligands  $L_1$  and  $L_0$ , e.g., 3- and 4-substituted styrenes, for which the Hammett relationship<sup>9</sup> is applicable, we can write, assuming that complexation is caused almost solely by the interaction of the olefinic bond with the silver ions as found in homogeneous silver(I) complexation<sup>10,11</sup>,

$$(\Delta G_M)_{L_1} - (\Delta G_M)_{L_0} = -2.3 RT \rho \sigma \quad (9)$$

where  $L_0$  refers to the unsubstituted ligand. Combination of eqns. 8 and 9 results in

$$\log \left[ \frac{(1/R_F^{\text{MS}} - 1)_{L_1}}{(1/R_F^{\text{S}} - 1)_{L_1}^\theta} \right] = \frac{n}{N} \rho \sigma + \log \left[ \frac{(1/R_F^{\text{MS}} - 1)_{L_0}}{(1/R_F^{\text{S}} - 1)_{L_0}^\theta} \right] \quad (10)$$

However, the plot of the logarithmic term *versus*  $\sigma$  gives a slope that is dependent on  $n/N$ . In order to determine the true  $\rho$  value, we must eliminate this factor. To a first approximation, we assume that  $R_F^{\text{M}}$  is correlated with  $R_F^{\text{MS}}$  and  $R_F^{\text{S}}$  according to the relationship

$$(1/R_F^{\text{M}} - 1) \approx \frac{N}{n} [(1/R_F^{\text{MS}} - 1) - \theta(1/R_F^{\text{S}} - 1)] \quad (11)$$

Substitution of eqn. 11 into eqn. 10 results in the following final expression:

$$\log [(1/R_F^{\text{MS}} - 1)_{L_1} - \theta(1/R_F^{\text{S}} - 1)_{L_1}] \approx \rho \sigma + \log \left[ \frac{n}{N} (1/R_F^{\text{M}} - 1)_{L_0} \right] \quad (12)$$

Eqn. 10 can be best used to test the linear free energy relationship, whereas eqn. 12 has to be applied to obtain the correct slope of the relationship found. Finally,  $\theta=1$  can be used in most instances, because most often  $(1/R_F^{\text{MS}} - 1)_L \gg (1/R_F^{\text{S}} - 1)$  and/or loading by M is small.

## RESULTS AND DISCUSSION

In the preparation of the silver nitrate-impregnated silica gel plates by immersing pre-coated silica gel plates in a solution of silver nitrate in acetonitrile, complete removal of the acetonitrile, as shown by infrared spectroscopy, was effected by drying the plates at 120° for 1 h. The blank silica gel plates were obtained in the same manner

using pure acetonitrile. Table I shows some data for the various silver nitrate-impregnated silica gel plates used.

TABLE I

DATA FOR SILVER NITRATE-IMPREGNATED SILICA GEL PLATES

<i>Loading</i> (g AgNO <sub>3</sub> /g silica)	<i>Solid AgNO<sub>3</sub><sup>*</sup></i> (relative figures)	<i>Surface area<sup>**</sup></i> (m <sup>2</sup> /g silica)
0.00		260
0.025		250
0.07	1	240
0.15	1	250
0.23	2.5	220
0.47	10	220

\* From X-ray diffraction measurements.

\*\* Nitrogen adsorption ( $\pm 10\%$ ).

The small decrease in the surface area of the stationary phase at the higher loadings of silver nitrate is the result of blocking of the micro-pores ( $< 30 \text{ \AA}$ ) of the silica by silver nitrate crystallites, as shown by the mercury penetration measurements and the fact that the surface area returns to its original value of  $260 \text{ m}^2/\text{g}$  after extraction of the silver nitrate by acetonitrile.

X-ray diffraction measurements indicate the presence of silver nitrate crystallites larger than  $10^3 \text{ \AA}$ . The relative intensities of the diffraction lines are not in agreement with those expected from the loading percentages and indicate the occurrence of an aqueous silver nitrate solution on the silica gel. This is well understood because the silica gel dried at  $120^\circ$  still contains  $8\%$  of water, which can dissolve  $0.18 \text{ g}$  of silver nitrate per gram of silica at room temperature. This result explains the large increase in the amount of solid silver nitrate at higher loadings (Table I). It is clear that the interaction of the ligand with the solid silver nitrate present is of minor importance because of its much smaller surface area (estimated silver nitrate surface area  $< 6 \text{ m}^2$  per gram of silica for the highest loading). Consequently, the complexation phenomena to be studied must be ascribed almost solely to the interaction of the ligand with the aqueous silver nitrate phase on the silica gel.

A series of 3- and 4-substituted styrenes was developed on the various silver nitrate-impregnated silica gel plates at  $25^\circ$  with chloroform as the eluent. The results are summarized in Table II.

Table III shows the reaction parameters  $n/N$ ,  $\rho$  and  $\rho$ , which were obtained from the data in Table II using eqns. 10 and 12 with  $\theta=1$ . The  $\sigma$  values used were derived from the Yukawa expression  $\sigma = \sigma^0 - r/|\sigma_R^+|$  (ref. 12) with  $r=0.44$ , using  $\sigma^0$  and  $|\sigma_R^+|$  values of Wepster and co-workers<sup>13,14</sup>. The choice of a resonance parameter  $r$  of 0.44 is somewhat arbitrary, viz., the mean value of  $r$  obtained from eqn. 10. The use of eqn. 12 in order to obtain the true  $\rho$  values gives a lower correlation coefficient than the use of eqn. 10, owing to both the approximation made in eqn. 11 to eliminate the  $n/N$  factor and the greater relative error in the term  $1/R_F^{\text{MS}} - 1/R_F^S$  with respect to  $(1/R_F^{\text{MS}} - 1)/(1/R_F^S - 1)$ . This latter cause is well demonstrated by the correlation co-

TABLE II

TLC DATA FOR SUBSTITUTED STYRENES ON SILVER NITRATE-IMPREGNATED SILICA GEL ( $R_F^{MS}$ ) AND SILICA GEL ( $R_F^S$ ) WITH CHLOROFORM AS THE ELUENT

Substituent	Loading (g AgNO <sub>3</sub> /g silica)							
	0.025		0.07		0.23		0.47	
	$R_F^{MS}$	$R_F^S$	$R_F^{MS}$	$R_F^S$	$R_F^{MS}$	$R_F^S$	$R_F^{MS}$	$R_F^S$
4-OMe	0.57	0.75	0.34	0.75	0.34	0.71	0.24	0.71
4-Me	0.66	0.81	0.47	0.79	0.44	0.78	0.35	0.76
H	0.68	0.79	0.51	0.77	0.48	0.77	0.39	0.74
3-OMe	0.61	0.74	0.48	0.75	0.45	0.71	0.37	0.71
3-Cl	0.73	0.80	0.65	0.79	0.65	0.78	0.58	0.77
3-NO <sub>2</sub>	0.67	0.73	0.61	0.73	0.62	0.70	0.55	0.69

TABLE III

$n \cdot X \cdot p$  AND  $p$  VALUES FOR THE SILVER(I) COMPLEXATION OF 3- AND 4-SUBSTITUTED STYRENES ON SILVER NITRATE-IMPREGNATED SILICA

Correlation coefficients are given in parentheses.

Equation	Parameter	Loading (g AgNO <sub>3</sub> /g silica)			
		0.025	0.07	0.23	0.47
10	$n \cdot X \cdot p$	-0.22 (0.98)	-0.49 (0.99)	-0.52 (0.99)	-0.59 (0.99)
12	$p$	-0.5 (0.89)	-0.74 (0.96)	-0.88 (0.97)	-0.82 (0.98)

efficients of the relationships from the silica impregnated with 0.025 g/g of silver nitrate, in which the  $R_F^{MS}$  and  $R_F^S$  values differ only slightly. The "true"  $p$  value from these data is therefore unreliable.

In conclusion, the results indicate a  $p$  value of  $-0.8 \pm 0.1$  for the complexation equilibria of substituted styrenes with silver(I). This value is very close to the  $p$  value of  $-0.77$  obtained by Fuens *et al.*<sup>10</sup> for the silver(I) complexation of substituted styrenes from direct solubility and distribution measurements. The results presented indicate that TLC is a useful additional technique for the quantitative determination of the strenghts of complexes<sup>1-8</sup>.

#### ACKNOWLEDGEMENTS

Nitrogen adsorption measurements were carried out by Mr. A. M. van Wijk of this Laboratory. Mercury penetration measurements were carried out by Mrs. L. A. de Wit and Mr. N. van Westen of the Laboratory of Chemical Technology. X-ray diffraction measurements were carried out by Mr. N. M. van der Pers of the Laboratory of Metallurgy.

## REFERENCES

- 1 F. R. Hartley, *Chem. Rev.*, 73 (1973) 163.
- 2 I. Jardine and F. J. McQuillin, *J. Chem. Soc., C*, (1966) 458.
- 3 F. Mikes, V. Schurig and E. Gil-Av, *J. Chromatogr.*, 83 (1973) 91.
- 4 W. S. Emerson, *Chem. Rev.*, 45 (1949) 347.
- 5 R. H. Wiley and N. R. Smith, *Org. Syn.*, 33 (1953) 62.
- 6 E. Stahl, *Dünnschicht-Chromatographie*, Springer, Berlin, 1967, p. 839.
- 7 E. Stahl, *Dünnschicht-Chromatographie*, Springer, Berlin, 1962, pp. 103-106.
- 8 M. Grimaldi, A. Liberti and M. Vicedomini, *J. Chromatogr.*, 11 (1963) 101 and references therein.
- 9 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 2nd ed., 1970.
- 10 T. Fueno, T. Okuyama, T. Deguchi and J. Furukawa, *J. Amer. Chem. Soc.*, 87 (1965) 170.
- 11 M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 84 (1962) 4697.
- 12 Y. Yukawa, Y. Tsuno and M. Sawada, *Bull. Chem. Soc. Jap.*, 39 (1966) 2274.
- 13 H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, 78 (1959) 815.
- 14 A. J. Heefnagel and B. M. Wepster, *J. Amer. Chem. Soc.*, 95 (1973) 5357.