

CHROM. 6877

## Note

---

### Identification of aromatic amides by reaction paper chromatography

JAROSLAV FRANC and KARLA POSPÍŠILOVÁ

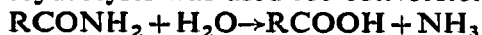
Research Institute of Organic Syntheses, Pardubice-Rybitví (Czechoslovakia)

(Received June 6th, 1973)

Recently we have investigated the use of reaction paper chromatography or paper electrophoresis (mainly, of course, in addition to reaction gas chromatography) for identification purposes. Some of the results have already been published<sup>1-3</sup>.

Basically, the difference in the mobility of the initial substance and the substance after reaction are used to determine the number of some of the functional groups present in the molecule. In this way, the number of carboxylic groups<sup>2</sup>, and the number of nitro groups on the aromatic ring<sup>3</sup>, for example, were determined. In this paper, the determination of the number of amide groups is described. The same procedure was used, *i.e.*, the initial substance (amide) was applied to the chromatogram next to the product formed by reaction (acid) and the difference in the  $R_F$  values was determined. From the magnitude of this difference, the presence of a certain number of  $-\text{CONH}_2$  groups was established; the procedure can possibly be used to prove the presence of a  $-\text{CONH}_2$  group.

Hydrolysis was used for conversion of the  $-\text{CONH}_2$  group into  $-\text{COOH}$ :



### EXPERIMENTAL AND RESULTS

#### *Hydrolysis of amides*

In a 5-ml ground-glass stoppered flask, one pellet of KOH is dissolved in 0.3 ml of diethylene glycol plus 0.2 ml of water. After cooling the flask, about 100 mg of the amide are added and a water-cooled condenser is connected to the flask. The flask is heated so that the mixture boils for 10 min, and the distillate is transferred into a flask containing 10 ml of 1% HCl. A further 3 ml of water are added during heating of this flask, and the heating is continued until the distillate is no longer alkaline. The acid is precipitated by acidification and washed thoroughly with water so as to remove potassium ions, which would interfere in the detection.

#### *Paper chromatography*

A suitable amount of a solution of the acid formed by hydrolysis is applied directly on the start of the chromatogram, and next to it is applied a 5% solution of the amide (unreacted) in dimethyl sulphoxide. Whatman No. 3 paper is used and developed by the descending technique with *n*-propanol-ammonia solution (2:1).

*Detection*

(I) *Spraying with mercuric acetate and diphenylcarbazone solutions.* Solution A consists of 1 g of mercuric acetate, 400 ml of ethanol and 10 drops of acetic acid, and solution B consists of 0.2 g of diphenylcarbazone and 400 ml of ethanol. The chromatogram is first sprayed with solution A and, after drying, with solution B until the purple background disappears. The spots of the substances remain purple.

(II) *Spraying with a saturated aqueous solution of 2,6-dichlorophenolindophenol.* After determining the appropriate  $R_F$  values,  $\Delta R_M$  values are calculated. The results are given in Table I. The number of  $-\text{CONH}_2$  groups present is derived from the  $\Delta R_M$  values.

TABLE I

 $R_F$  VALUES OF AMIDES AND THE CORRESPONDING ACIDS

Paper chromatography on Whatman No. 3 paper with *n*-propanol-ammonia solution (2:1)

Compound	$R_F$	$R_M$	$\Delta R_M^*$			Detection**	
			I	II	III	I	II
Benzoic acid	0.67	-0.31				+	+
Benzamide	0.86	-0.79	0.48			+	-
Phthalic acid	0.32	+0.33				+	+
Phthalodiamide	0.66	-0.29		0.62		+	-
Isophthalic acid	0.29	+0.39				+	+
Isophthalodiamide	0.69	-0.35		0.74		+	-
Terephthalic acid	0.23	+0.53				+	+
Terephthaloamide	0.50	0.00	0.53			+	+
Terephthalodiamide	0.62	-0.21		0.74		+	-
Toluyllic acid	0.75	-0.48				-	+
Toluylamide	0.89	-0.91	0.43			+	-
<i>p</i> -Cyanobenzoic acid	0.72	-0.41				+	+
<i>p</i> -Cyanobenzamide	0.90	-0.95	0.54			+	-
Salicylic acid	0.76	-0.50				+	+
Salicylamide	0.65	-0.27	-0.23			+	-
Trimellitic acid	0.08	+1.10				+	+
Monoamide of trimellitic acid	0.16	+0.72	0.38			+	+
Diamide of trimellitic acid	0.30	+0.37		0.72		+	+
Triamide of trimellitic acid	0.44	+0.10			0.99	+	-

\* I, II and III denote one, two and three  $-\text{CONH}_2$  groups, respectively.

\*\* Detection methods I and II, see text.

## DISCUSSION

The results in Table I were plotted graphically (Fig. 1). It can be seen that there is a linear dependence between the number of  $-\text{CONH}_2$  groups and the  $\Delta R_M$  values, *i.e.*, the difference in the mobilities of the initial amide and the acid formed by the

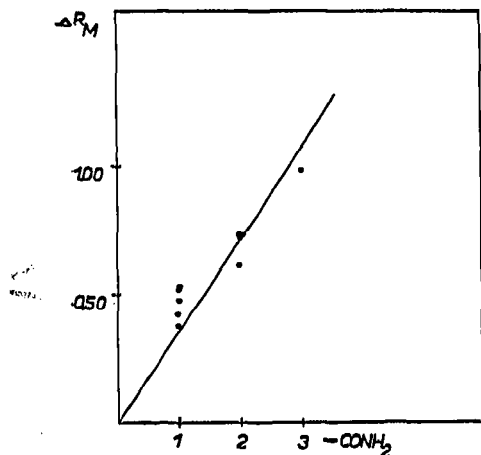


Fig. 1. Plot of  $\Delta R_M$  against the number of  $-\text{CONH}_2$  groups present.

reaction. From the results, the average  $\Delta R_M$  values are  $+0.47$  for one,  $+0.71$  for two and  $+0.99$  for three  $-\text{CONH}_2$  groups. Salicylamide and salicylic acid formed by its hydrolysis ( $\Delta R_M = -0.23$ ) are exceptions, owing to the strong hydrogen bonding between the hydroxy and carboxy groups of salicylic acid. We encountered a similar effect with *ortho*-substituted carboxylic acids<sup>2</sup> during the determination of the number of  $-\text{COOH}$  groups present. If a shift in  $R_M$  of  $+0.68$  is considered for a hydrogen bridge, then an  $R_M$  of  $+0.75$  is obtained for one  $-\text{CONH}_2$  group for salicylic acid, which is in agreement with the results obtained.

This short paper is another contribution to our overall programme to develop a series of methods for determining the number of different functional groups in molecules by using reaction paper chromatography (or electrophoresis).

#### REFERENCES

- 1 J. Franc and K. Pospíšilová, *J. Chromatogr.*, 48 (1970) 207.
- 2 J. Franc and K. Pospíšilová, *J. Chromatogr.*, 66 (1972) 329.
- 3 J. Franc and K. Pospíšilová, *J. Chromatogr.*, 74 (1972) 157.