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REACTION PAPER CHROMATOGRAPHY OF CARBOXYLIC ACIDS WITH THE USE OF ELECTROLYTIC REDUCTION

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SUMMARY

A method was developed, combining reaction paper chromatography with electrolytic reduction, for the determination of the presence of –COOH groups and possibly their number by comparing the R_F values before and after reaction. Moreover, in the solvent system used (*n*-propanol–ammonia), it is possible to assess the presence of other functional groups from the shift in the R_F values.

INTRODUCTION

When identifying organic substances, it is in some cases necessary to determine the number of carboxyl groups present in carboxylic acids. If no other groups are present in the molecule, this information can be obtained, for instance, by paper electrophoresis[1] or from the R_F values, or possibly quantitatively after decarboxylation[2]. However, both electrophoresis and paper chromatography are interfered with by the presence of other functional groups that are capable of establishing intermolecular hydrogen bridges, such as $-SO_3H$, $-OH$, $-NH_2$ and $-CONH_2$, as these functional groups affect both the mobility in electrophoresis and the R_F value in paper chromatography.

However, the carboxyl group can be reduced electrolytically to the aldehyde or possibly down to the corresponding alcoholic function. A number of studies dealing with this problem have already been described[3–13]. Many of them, however, make use of substitution reactions, which are unsuitable for our purpose. The most suitable procedure was that described by METTLER[3], who obtained the corresponding aldehydes from certain aromatic carboxylic acids without partitioning the anode and cathode compartments. The preparation of the electrodes used was also simple.

EXPERIMENTAL

The procedure described by METTLER[3] was adapted for our purposes. The electrolyte used contained 6 g of boric acid and 6 g of sodium sulphate in 100 ml of water. The aromatic acids to be analyzed were dissolved in a minimum amount of

10–15% aqueous sodium carbonate solution. The analysis was performed with a solution in the electrolyte, the volume of which corresponded to a sample solution with a concentration of about 5%. A mercury cathode and a platinum anode were used as electrodes. The electrolytic reduction was carried out in a small glass reactor (Fig. 1). The platinum anode (2) is formed from a small platinum sheet situated at the wall of the electrolytic vessel, and the cathode (1) is mercury situated in the bottom of the reactor and in a side branch, where a platinum wire (3) and a copper wire (6) dip into the mercury. The reaction vessel is provided with a drain tap (4) at the bottom.

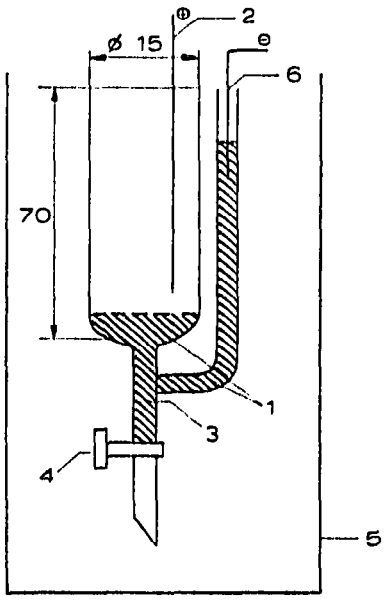


Fig. 1. Glass reactor for the electrolytic reduction of carboxylic acids. The parts are identified in the text.

The electrolytic reduction is carried out as follows. About 5 ml of electrolyte are introduced on to the mercury in the bottom of the vessel and the sample solution is added about 1/2 min after switching on the current. The electrolysis is allowed to proceed for 10 min (in exceptional cases for 30 min). As the solution is strongly heated by the passage of current, the entire reactor vessel is immersed in a vessel (5) supplied with flowing cooling water. In spite of this, the temperature in the reactor becomes quite high, about 50–80°. At an electrode potential of 12 V the current varies from 1.8 to 2A.

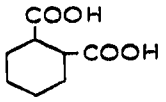
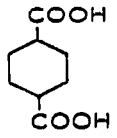
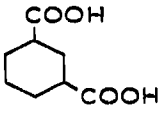
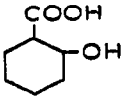
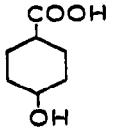
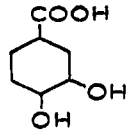
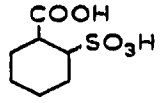
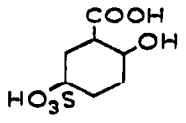
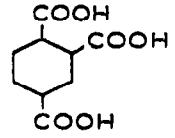
The current is switched off after 10 min and the electrolyte is used directly for application on to the chromatography paper. Whatman No. 3 paper is used in an *n*-propanol–ammonia (2:1) solvent system. About 10–15 μl of the sample are applied, simultaneously with the original non-electrolyzed sample.

After the conclusion of the separation, the paper strip with the original sample is sprayed with 2,6-dichlorophenolindophenol (saturated aqueous solution) and the paper strip with the electrolyzed sample is treated with 2,4-dinitrophenylhydrazine (saturated solution in 2 *N* hydrochloric acid). When other functional groups are also to be studied, use can be made of other suitable detection agents.

The shift in the R_F values of the aldehydes formed is determined in terms of the R_F value of the original substance. The R_F values and the shifts due to electrolytic reduction are listed in Table I.

TABLE I

R_F VALUES OF CARBOXYLIC ACIDS BEFORE AND AFTER ELECTROLYTIC REDUCTION
Whatman No. 3 paper; *n*-propanol–ammonia (2:1) solvent.

	Substance	R_F				ΔR_M		
		Original substance	*I spots*	*II spots*	*III spots*	*I spots*	*II spots*	*III spots*
1		0.27	0.65	0.83		−0.70	−1.12	
2		0.26	0.61	0.87		−0.64	−1.27	
3		0.27	0.65	0.87		−0.70	−1.25	
4		0.72	0.85			−0.35		
5		0.38	0.73			−0.64		
6		0.15	0.53			−0.81		
7		0.27	0.70			−0.80		
8		0.37	0.55			−0.30		
9		0.06	0.25	0.75	0.90	−0.74	−1.70	−2.17

(Continued on p. 332)

TABLE I *(continued)*

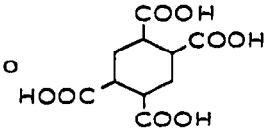
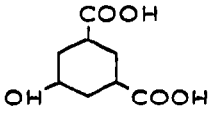
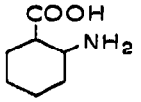
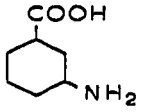
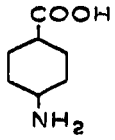
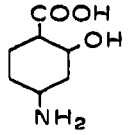
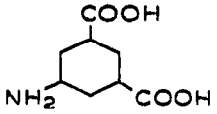
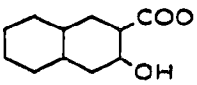
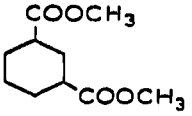
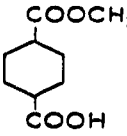
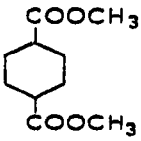
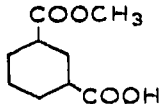
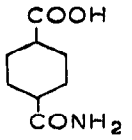
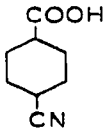
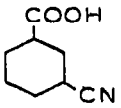
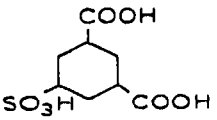
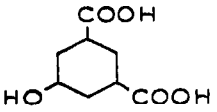
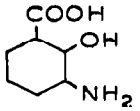
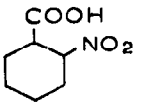
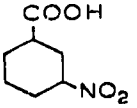
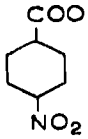
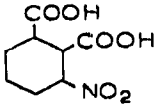
Substance	R_F				ΔR_M		
	Original substance	*I spots*	*II spots*	*III spots*	*I spots*	*II spots*	*III spots*
10 	0.01	0.09	0.24	0.38 (weak)	−0.89	−1.41	−1.70
11 	0.05	0.22	0.57 (weak)		−0.75	−1.42	
12 	0.60	0.84			−0.55		
13 	0.47	0.84			−0.78		
14 	0.44	0.82			−0.76		
15 	0.46	0.77			−0.60		
16 	0 11	0.23			−0.38		
17 	0.80	0.87			−0.23		
18 	0.27[a] (0.94)	0.69 (weak)	0.87		−0.78		
19 	0.26[a] (0.70)	0.61			−0.64		
20 	0.26[a] (0.94)	0.62 (weak)	0.87		−0.66	−1.28	

TABLE I *(continued)*

Substance		R_F				ΔR_M		
		Original substance	*I spots*	*II spots*	*III spots*	*I spots*	*II spots*	*III spots*
21		0.27 (0.64)	0.63	0.89		−0.66	−1.34	
22		0.26 (0.42)	0.88				−1.31	
23		0.68	0.93 (weak)			−0.83		
24		0.66	0.90			−0.66		
25		0.15	0.27			−0.33		
26		0.05	0.22	0.57 (weak)		−0.75	−1.42	
27		0.48	0.83			−0.73		
28		0.61	0.29[b] (weak)	0.88		+0.48[b]	−0.67	
29		0.69	0.45[b]	0.84		+0.41[b]	−0.37	
30		0.70	0.39[b]	0.89		+0.56[b]	−0.54	
31		0.27	0.16[b]	0.31[b]	0.86[b] (weak)	+0.29[b]	−0.08[b]	−1.22[b]

[a] Value computed with respect to the corresponding acid.
[b] Positive reaction with Ehrlich reagent.
(weak) = weak spot.

RESULTS AND DISCUSSION

The results of the present method show that electrolytic reduction can be used advantageously for the identification of benzenecarboxylic acids which may be substituted by further functional groups, because the difference between R_F (R_M) values before and after the reaction can be utilized for this purpose. On average, this shift for one –COOH group amounts to $R_M = -0.75$ ($R_F = +0.37$), for two –COOH groups $R_M = -1.33$, and for three such groups $R_M = -1.94$. The only exception is represented by such cases where an –OH or $-NH_2$ group is in the *ortho* position with respect to the –COOH group (a shift of $R_M = -0.23$ to -0.60). Formation of the –CHO group is proved by the reaction with 2,4-dinitrophenylhydrazine. When the benzene nucleus is substituted by more –COOH groups, intermediate stage products are usually formed.

Paper chromatography in *n*-propanol–ammonia (2:1) has the advantage that substances are separated according only to their ability to form intermolecular hydrogen bridges between the functional group and the developing solvent system, whereas the actual position of the functional group on the aromatic nucleus is not decisive. Moreover, the R_F value makes it possible to assess the number of polar groups and the presence of others. Table II indicates the shifts in the R_M values that are caused by the presence of various functional groups (relative to benzoic acid), so that the use of these values may give further information on the acid to be identified.

TABLE II

THE SHIFT OF R_F VALUES DUE TO VARIOUS FUNCTIONAL GROUPS IN *n*-PROPANOL–AMMONIA (2:1), R_F = 0.70 OF BENZOIC ACID BEING TAKEN AS BASE VALUE

Functional group	ΔR_M
–COOH	+0.88
–CHO	−0.75
–OH	+0.60
$-NO_2$	0.00
$-SO_3H$	+0.86
$-NH_2$	+0.50
$-COOCH_3$	−0.10
$-COHN_2$	+0.56
–CN	+0.06

Some complication arises from the presence of an $-NO_2$ group as this is electrolytically reduced to an $-NH_2$ group, so that a further spot usually appears on the chromatogram. This, however, can be easily identified because the $-NH_2$ group gives the characteristic reaction with the Ehrlich reagent.

The method is not suitable for acids that produce volatile aldehydes, which volatilize from the paper, such as benzoic acid and most of the lower aliphatic acids.

Acids having more than three –COOH groups cannot be converted completely to the corresponding aldehyde groups, even by prolonged electrolytic reduction; this is the case, for instance, with benzene-1,2,4,5-tetracarboxylic acid and naphthalene-1,4,5,8-tetracarboxylic acid.

In spite of these shortcomings, the method of electrolytic reduction combined with paper chromatography is believed to be a suitable technique for the identification of benzenecarboxylic acids.

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