PAPER CHROMATOGRAPHY OF SOME ISOMERIC MONOSUBSTITUTED PEROXYBENZOIC ACIDS

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INTRODUCTION

As part of our program on peroxy acids we have prepared and investigated the paper chromatographic separation of some isomeric monosubstituted peroxybenzoic acids in order to obtain information about the *ortho* effect and other structural factors influencing the properties of these compounds. The problem is a complex one, because in addition to factors such as inductive and steric effects, field and resonance, several implications of hydrogen bonding must be considered, including solvation and intramolecular (chelation) effects, as well as intermolecular associations (dimerization)[1,2,3]. Consequently, it is to be expected that the so-called *ortho* effect may vary markedly under different conditions.

Reviewing the literature on the paper chromatography one notes that aromatic peroxy acids have been ignored in the many recent applications of this technique. In general, the reports have concerned themselves with the paper chromatography of organic peroxides. Thus, RIECHE AND SCHULZ[4] were first to report on the separation of various organic peroxides and used ethyl acetate–dioxane–water (2.0:4.5:4.6) as the mobile solvent on partially acetylated paper (20%) and a solution of *p*-aminodimethylaniline hydrochloride in methanol as spray reagent for locating peroxides. ABRAHAM and coworkers[5] used paper treated with silicone oil, the mixture ethanol–chloroform–water as the mobile phase and a solution of ferrothiocyanate as a spraying agent. MILAS AND BELIČ[6] have obtained good results for identification and separation of the organic peroxides on unimpregnated paper using dimethylformamide–decalin, N-methylformamide–decalin–*n*-butanol (45%), and ethanol–water as the mobile solvents. CARTLIDGE AND TIPPER[7] were successful in avoiding the losses due to the volatility of the organic peroxides during the chromatographic separation by covering the chromatographic paper with two glass plates. They used a mixture of water–diethyl ether–*n*-butanol (1:10:10) for chromatography of organic peroxides on unimpregnated paper. A mixture of water–ethanol–chloroform (20:17:2) was recommended as the mobile phase on paper impregnated with silicone oil and *n*-butanol–petroleum ether (b.p. 80–100°) as the mobile solvent on paper impregnated with ethylene glycol. DOBSON AND HUGHES[8] used paper impregnated with a 5% solution of silicone oil in petroleum ether (b.p. 80–100°) for paper chromatography of dialkyl peroxides and water–methanol as the mobile solvent. In the paper by CARTLIDGE AND TIPPER[7] the data on R_F values for lower aliphatic acids from C_1 to C_4 are also given.

This paper describes a simple procedure for the paper chromatography of isomeric monosubstituted peroxybenzoic acids and presents an attempt to investigate the effect of the orientation of substituent groups on the R_F values. Data are presented for some known aromatic peroxybenzoic acids and for a number of monosubstituted peroxybenzoic acids which have not been previously prepared.

EXPERIMENTAL

A series of isomeric monosubstituted peroxybenzoic acids was prepared for this purpose, by thus extending SWERN's procedure[9]. Crude peracids were recrystallised or purified by sublimation *in vacuo*. Thoroughly dried peracids were used then without further purification. Gas phase chromatography of peroxy acids thus prepared indicated that they contained no isomers. The chromatographic papers used were: partially acetylated paper for chromatography from Binzer (25 % acetylation), Schleicher & Schüll paper No. 2043b, and a paper impregnated in this laboratory. The latter was impregnated by standing overnight in a 20 % solution of N-methylformamide in acetone and dried in air. All chromatograms were run at 25° using the ascending technique. The papers were allowed to equilibrate 30 min in the tank before immersion. The solvents were allowed to travel 17 cm requiring 30 to 60 min. The paper sheets were sprayed with the spray reagent as soon as they were removed from the tanks and then air dried.

RESULTS AND DISCUSSION

Hexane–dioxane–dimethylformamide (25:12:12) were found to be a satisfactory mobile solvent for use in the paper chromatography of isomeric monosubstituted peroxybenzoic acids on acetylated paper using ascending development. The mixture of these solvents was vigorously shaken and allowed to stand in a separatory funnel for 3 to 4 h. A solution of hexane saturated with dioxane and dimethylformamide was used as mobile phase. Benzene was found to be satisfactory as mobile phase in the paper chromatography of the above mentioned peroxy acids on paper impregnated with N-methylformamide.

A solution of *p*-aminodimethylaniline hydrochloride in methanol (10 ml water:10 ml ethanol:1 ml glacial acetic acid:1 g reagent) was found to be a good spot-locating reagent. The solution is quite stable and gives easily discernible red-coloured spots. These spots are not permanent and disappear after a certain period of time. A solution of potassium iodide and a starch solution (5 ml of glacial acetic acid, 5 ml of a saturated solution of potassium iodide and 5 ml of a 5 % starch solution) has also been found to be a very good spray reagent. It gives black spots which are permanent, so that the paper chromatograms may be retained as a record.

Chromatographic data for various isomeric monosubstituted peroxybenzoic acids are summarized in Table I. Migration rates are given in R_b values, where R_b is the migration distance of the peroxy acid divided by the migration distance of the unsubstituted peroxybenzoic acid. The R_F values of peroxybenzoic acid averaged about 0.35 on acetylated paper and 0.36 on impregnated paper.

A comparison of the effect of isomeric groups on the separation in the first solvent shows that, in general, the lowest R_b values are obtained with *ortho* isomers. The

TABLE I

R_b VALUES* OF ISOMERIC MONOSUBSTITUTED PEROXYBENZOIC ACIDS

Peroxy acid	R_b	
	*I***	*II****
o-Chloroperoxybenzoic	0.51	1.17
m-Chloroperoxybenzoic	0.91	1.30
p-Chloroperoxybenzoic	0.80	1.42
o-Bromoperoxybenzoic	0.66	1.06
m-Bromoperoxybenzoic	1.23	1.20
p-Bromoperoxybenzoic	1.14	1.42
o-Nitroperoxybenzoic	0.11	0.33
o-Fluoroperoxybenzoic	0.57	0.89
p-Fluoroperoxybenzoic	0.10	1.06
m-methylperoxybenzoic	1.57	1.53
p-methylperoxybenzoic	1.31	1.36

* $R_b = \frac{\text{Migration distance of substituted peroxybenzoic acid}}{\text{Migration distance of peroxybenzoic acid}}$.

** 25% acetylated paper; solvent: hexane saturated with dioxane and dimethylformamide.

*** Paper impregnated with N-methylformamide; solvent: benzene.

meta isomers have the greatest R_b values. The difference in R_b values between *meta* and *para* isomers are relatively small. The so-called *ortho* effect is quite obvious among the isomeric groups. The *ortho* isomer is separate from the *meta* and *para* isomers. The R_b values of the *meta* and *para* isomers are close together, with the *meta* isomer having a slightly greater R_b value than the *para* isomer. The only exception is *m*-methyl peroxybenzoic acid which has a higher R_b value. The differences in R_b values of various isomeric groups on different chromatographic papers and/or in different solvents show many variations depending on the nature of the substituting groups and the solvents. For example, in both mobile solvents, the chloro-peroxybenzoic acids show large R_b differences between the isomers. The methyl peroxybenzoic acids, however, show little difference in R_b values in both solvents. The fluoro-peroxybenzoic acids, on the other hand, show the largest differences in the first system of mobile solvents.

Observation of the data in Table I, column II, shows that when benzene was used as the mobile phase on impregnated paper, the order is altered, for *meta* and *para* substituted peroxybenzoic acids, the *para* isomer having the higher R_b value. With the three isomers, there is a large difference between the *ortho* and *para* isomers while the *ortho* and *meta* isomers run close together.

If methanolic solutions of a monosubstituted peroxybenzoic acid were used in the paper chromatography 3 to 5 spots were detected after the development of the chromatograms. In order to elucidate this, some qualitative experiments using thin-layer chromatography were carried out and a considerably sharper separation of these spots of substances with similar R_b values was obtained. The origin of these spots is presumably due to reaction products formed between the peroxy acid and the alcohol. The explanation of this phenomenon will be the subject of a forthcoming publication.

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SUMMARY

The R_b values of a number of isomeric monosubstituted peroxybenzoic acids have been determined for two different solvent systems. The solvent systems are hexane saturated with dioxane and dimethyl formamide for use on acetylated paper and benzene for use on paper impregnated with N-methylformamide. The R_b values of isomeric peracids vary considerably, depending on the substituent group and its orientation. An attempt is made to correlate the chromatographic data with the structure of the compounds. The influence of the strong inductive and steric effects of the substituents is clearly seen.

REFERENCES

1 D. SWERN, L. P. WITNAUER, C. R. EDDY AND W. E. PARKER, *J. Am. Chem. Soc.*, 77 (1955) 5537.
2 D. BELITSKUS AND G. A. JEFFREY, *Acta Cryst.*, 18 (1965) 458.
3 M. SAX, P. BEURSKENS AND S. CHU, *Acta Cryst.*, 18 (1965) 252.
4 A. RIECHE AND M. SCHULZ, *Angew. Chem.*, 70 (1958) 694.
5 M. H. ABRAHAM, A. G. DAVIES, D. R. LLEWELLYN AND E. M. THAIN, *Anal. Chim. Acta*, 17 (1957) 499.
6 N. A. MILAS AND I. BELIČ, *J. Am. Chem. Soc.*, 81 (1959) 3358.
7 J. CARTLIDGE AND C. F. H. TIPPER, *Anal. Chim. Acta*, 22 (1960) 106.
8 G. DOBSON AND G. HUGHES, *J. Chromatog.*, 16 (1964) 416.
9 L. S. SILBERT, E. SIEGEL AND D. SWERN, *J. Org. Chem.*, 27 (1962) 1336.