

On the Paper Chromatography of the Salts of Organic Bases.

By Teiji Ukai and Tsutomu Ohashi.

Tatsuo Kariyone and his associates have found that Dragendorff's reagent can be used for developing the spots of the basic substances.

First the present authors intended to utilize the photosensitivity of silver halides, which are produced by the action of AgNO_3 or KAgCO_3 on the halides of different bases.

The solvent was the mixture of butanole, $\text{CH}_3\cdot\text{COOH}$ and H_2O (60:40:35).

The paper used was Toyo-Filter Paper No. 131 in $2 \times 40\text{cm}$. strips. Water

solutions of the halides of the bases were spotted on the strips and the solvent was allowed to descend for 12 hours at $6-11^\circ$. The spots were developed by spraying either with 5% AgNO_3 or with the saturated solution of KAgCO_3 and K_2CO_3 in water, drying them at room temperature and subjecting them to the light.

In the case of iodides the spot also can be traced by H_2O_2 which causes iodine-starch reaction.

The results obtained are shown in Table I.

Table. I.

Halide of bases	Rf calcted from the spot of halogen
o-Toluidine HCl	0.15
p-Toluidine HCl	0.15
o-Toluidine HBr	0.14
m-Toluidine HBr	0.15
p-Toluidine HBr	0.17
Semicarbazide HCl	0.18
Aniline HI	0.19
Methylaniline HI	0.21

But as a question was raised whether the spot of the halogen might show the position of the base itself or not, we

sought the spots of the bases by color reactions.

Table. II.

Halides of bases	Rf calcted from the spot of halogen	Rf calcted from the spot of the base itself by color reaction
Dimethylaniline HI	0.24	0.90
Methyliodide of Dimethylaniline	0.33	0.83
Methyliodide of chinoline	0.21	0.76
Methyliodide of isochinoline	0.21	0.86
Pyridine HI	0.17	0.80
Histidine HCl	0.14	0.24
Glycine HCl	0.14	0.67
P. A. S. HCl	0.22	0.89

From Table II it is clear that Rf of the halogen in a certain halide is quite different from that of the base.

We found then that even when the mixture of two chlorides was used, only one spot of the halogene could be seen by AgNO_3 -method at a different place from those of the corresponding halides. This fact raised another doubt in our minds if the position of the spot of a

base developed from the mixture of halides were the same with the one originated from a halide of that base. So we investigated the spots of the bases in the mixture of two halides by color reactions. Table III shows Rf of the halogen and that of the base in several halides which were spotted either alone or combined with another halide.

Table. III.

	Rf calcted from the spot of Cl.	Rf calcted from the spot of the base.	Rf calcted from the spot of the base by color reaction when its halide is mixed with another halide.								
			(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
(1)	0.24	0.45	...	0.42	0.42		0.42			0.40	0.41
(2)	0.24	0.59	0.64	...	0.62	0.54	0.70	0.69	0.67	0.67	0.65
(3)	0.18	0.62	0.62	0.64	...	0.63		0.62	0.61		0.62
(4)	0.18	0.87	0.88	0.84	0.81	...	0.87			0.85	0.83
(5)	0.19	0.53	0.52	0.60		0.61	...	0.60	0.58		0.59
(6)	0.22	0.86	0.82	0.80	0.85		0.85	...	0.83	0.80	0.84
(7)	0.22	0.72	0.78	0.86	0.71		0.73	0.73	...		
(8)	0.17	0.83	0.83	0.83		0.84		0.81		...	0.81
(9)	0.18	0.41	0.41	0.41	0.42	0.42	0.42	0.43		0.42	...

(1) . . .HCl salt of hydroxylamine.

(3) . . . " p-nitroso-dimethylaniline.

(5) . . . " vitamin B₁.

(7) . . . " aniline.

(9) . . . " semicardazide.

(2) . . .HCl salt of p-amino dimethylaniline.

(4) . . . " chinoline.

(6) . . . " pyridine.

(8) . . . " o-toluidine.

As shown in Table III, when hydrochloride of p-amino-dimethylaniline was mixed with hydrochloride either of aniline or of pyridine, Rf of the former was quite different from its proper one.

We improved then the method by

adding the same acid with the component of the salt to the solvent. Thus satisfactory results were obtained for the analytical purpose as shown in Table IV and V.

Table. VI.

Rf of acetate of p-amino-dimethylaniline	0.73
" when mixed with pyridine	0.77
" when mixed with aniline	0.76
Solvent (Butanole 60 : $\text{CH}_3\text{-COOH}$ 40 : H_2O 35)	

Table. V.

Rf of chloride of p-amino-diaethylaniline	0.91
„ when mixed with chloride of pyridine	0.90
„ when mixed with chloride of aniline	0.90
Solvent (Butanole 85 : 5% HCl 15)	

SUMMARY The paper chromatography of the salts of the bases was improved by adding the same acid with the component of the salts to the solvent. (Received, march 20)