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THE ANALYTICAL REACTIONS OF THE PERBROMATE ION

II. SPOT TESTS, PARTITION AND ION-EXCHANGE THIN-LAYER CHROMATOGRAPHY

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SUMMARY

Spot tests and partition and anion-exchange thin-layer chromatography data for the perbromate ion are given. The sequence of the perhalo acids in the various systems is discussed.

INTRODUCTION

Preliminary studies on the separation of perbromate from other halo acids were reported earlier from this laboratory¹ and the aim of that work was to observe the electrophoretic and chromatographic movement of perbromate in relation to other acids of the halogens.

The present work is an extension of these studies, in which the main purpose was to provide analytical data of such spot tests, partition chromatography systems and ion-exchange systems, which are commonly used for the identification and separation of halo acids.

SPOT TESTS

We have tried to survey the various spot tests for bromate, iodate, periodate and chlorate, and we wished to establish where perbromate would give a positive reaction, in order to provide spot reactions for perbromate and also to determine where perbromate would interfere with the spot tests for the other halo acids.

Test with manganous sulphate and phosphoric acid

In a concentrated solution of phosphoric acid, chlorates warmed with manganese sulphate form a more or less deep violet coloration². Perbromate was also found to yield a violet coloration, as did bromate and periodate.

Test with manganous sulphate and sulphuric acid²

When a drop of a sample is heated with a drop of 2% manganous sulphate solution acidified with a small amount of sulphuric acid and warmed for 2-3 min on

TABLE I

SPOTS TEST REACTIONS OF HALO ACIDS

Ion	Manganous sulphate + phosphoric acid	Manganous sulphate + sulphuric acid	Acidified KCNS	Acidic pyrogallol	Potassium iodide in HCl	Methylene blue
BrO_4^-	+	-	-	-	+	+
BrO_3^-	+	+	-	+	+	-
IO_4^-	+	-	-	-	+	-
IO_3^-	-	-	+	+	+	-
ClO_4^-	-	-	-	-	-	+
ClO_3^-	+	-	-	-	+	+

TABLE II

 R_F VALUES OF HALO ACIDS ON WHATMAN No. 1 PAPER

Solvent: mixtures of isopropanol and 1.5 N ammonia solution.

Ion	Ratio of isopropanol to 1.5 N ammonia solution												
	95:5	90:10	80:20	70:30	65:35	60:40	55:45	50:50	40:60	30:70	20:80	10:90	5:95
ClO_3^-	0.19	0.34	0.48	0.59	0.67	0.71	0.74	0.80	0.80	0.80	0.85	0.88	0.93
BrO_3^-	0.05	0.07-0.19	0-0.33	0.26-0.44	0.50	0.56	0.62	0.64	0.73	0.75	0.80	0.90	0.93
IO_3^-	0.00	0.00	0.04	0.14	0.23	0.30	0.36	0.47	0.52	0.63	0.76	0.83	0.86
ClO_4^-	0.30	0.42	0.54	0.58-0.70	0.70	0.72	0.72	0.77	0.77	0.80	0.84	0.84	0.85
BrO_4^-	0.40	0.50	0.64	0.78	0.78	0.82	0.84	0.81	0.84	0.83	0.85	0.88	0.94
IO_4^-	0.00	0.00	0.04	0.16	0.26	0.31	0.40	0.53	0.54	0.65	0.76	0.80	0.85

^a ↓ = comet.

a water-bath, a red colour is formed initially, which on boiling becomes a precipitate of brown manganese hydroxides. Only bromate reacts under these conditions, and perbromate, iodate, periodate, chlorate and perchlorate do not give positive reactions.

Test with potassium thiocyanate²

In acidic solution, iodate reacts with potassium thiocyanate to liberate iodine. No coloration is given by bromate or perbromate.

Test with pyrogallol²

In acidic solution, iodates oxidise pyrogallol to purpurogallin. Strong oxidising agents, such as iodine and chromate, act in the same way. Persulphate, nitrate and bromate give similar colours, which can be distinguished if parallel tests are made. Perbromate does not give a coloration in this test.

Reaction with potassium iodide in hydrochloric acid

We have already reported that while bromate, iodate and periodate react instantaneously with this reagent, perbromate reacts rather slowly¹. Chlorate will yield a spot of iodine only in HCl of concentration above 6 *N*. Perchlorate does not react. As this test is one of the two most suitable tests for detection on chromatograms, we determined its sensitivity for perbromate by spraying spots of dilute solutions, either simply placed on the paper or after chromatographic development. Spots placed directly on the paper could be detected when they contained $2 \cdot 10^{-5}$ *M* perbromate; after development, spots of 10^{-3} *M* concentration could still be detected.

Samples of perbromate with excess of KI in dilute HCl were also placed in the spectrophotometer and the time required for maximum colour development was measured. The reaction slowed considerably after 4 h but even then the amount of iodine liberated does not correspond to complete reduction.

We intend to study this reaction in more detail later.

Reaction with methylene blue

Methylene blue is the other reagent which lends itself readily to detection on chromatograms and electropherograms. A red spot is given by perchlorate and by perbromate as well as by numerous poorly hydrated anions. The sensitivity of methylene blue was determined for spots placed on paper; $6 \cdot 10^{-3}$ *M* solutions could still be detected. After development, 10^{-2} *M* solutions still yielded visible spots.

The spot reactions of perbromate and the other halo acids are summarised in Table I.

PARTITION CHROMATOGRAPHY

The partition systems for inorganic anions for which most data have been published are *n*-butanol-1.5 *N* ammonia solution, *n*-butanol-pyridine-1 *N* ammonia solution and mixtures of isopropanol and 1.5 *N* ammonia solution in various proportions^{3,4}.

The behaviour of perbromate in the first two solvents was studied by LEDERER AND SINIBALDI¹; extensive reduction was noted on filter-paper and thin layers of cellulose and none on thin layers of silica gel.

TABLE III

R_F VALUES OF HALO ACIDS ON CELLULOSE THIN LAYERS
Thin layer: Macherey-Nagel Cell 300. Solvent: mixtures of isopropanol and 1.5 N ammonia solution.

Ion	Ratio of isopropanol to 1.5 N ammonia solution										
	95:5	90:10	80:20	70:30	60:40	50:50	40:60	30:70	20:80	10:90	5:95
ClO_3^-	0.02	0.34	0.65	0.74	0.84	0.85	0.92	0.90	0.90	0.90	1.00
BrO_3^-	0.05	0.16	0.33	↓ ^a 0.29 0.54	0.70	0.74	0.84	0.84	0.88	0.88	0.95
IO_3^-	0.07	0.03	0.10	0.00 ↓ 0.42	0.42 ↓ 0.60	0.56	0.00 ↓ 0.70	0.70	0.78	0.90	0.94
ClO_4^-	0.02	0.35	0.62	0.30 0.64-0.83 0.62	0.86 0.75	0.89	0.83	0.80	0.84	0.93	0.90
BrO_4^-	0-0.70	0.67	0.76	↓ 0.87	↓ 0.91	0.86	0.81	0.84	0.84	0.92	0.91
IO_4^-	0.02	0.00	0.10	0-0.30	0.00 ↓ 0.55	0.00 ↓ 0.60	0.00 ↓ 0.61	0.00 ↓ 0.70	0.00 ↓ 0.79	0.00 ↓ 0.93	0.89

^a ↓ = comet.

TABLE IV

R_F VALUES OF HALO ACIDS ON SILICA GEL THIN LAYERS
Thin layer: Macherey-Nagel SIL G. Solvent: mixtures of isopropanol and 1.5 N ammonia solution.

Ion	Ratio of isopropanol to 1.5 N ammonia solution										
	95:5	90:10	80:20	70:30	60:40	50:50	40:60	30:70	20:80	10:90	5:95
ClO_3^-	0.53	0.57	0.67	0.62	0.64	0.76	0.84	0.85	0.92	0.87	0.85
BrO_3^-	0.44	0.47	0.48	0.61	0.71	0.76	0.76	0.85	0.85	0.90	0.91
IO_3^-	0.04	0.08	0.21	0.33	0.36	0.51	0.66	0.70	0.80	0.86	0.76
ClO_4^-	0.20-0.49	0.62	0.66	0.67	0.76	0.80	0.78	0.88	0.91	0.93	0.93
BrO_4^-	0.71	0.75	0.77	0.76	0.79	0.86	0.88	0.90	0.90	0.92	0.92
IO_4^-	0.02	0.02	0-0.21	0.02	0.03	0.02	0-0.65	0-0.17	0.02-0.16	0-0.90	0-0.73

We report here R_F values for isopropanol-1.5 *N* ammonia mixtures on filter-paper (Table II) and thin layers of cellulose (Table III) and silica gel (Table IV). There was some reduction of the perbromate (comets) on cellulose paper and thin layers, but none on the thin layers of silica gel. Hence the data in Tables II and III serve mainly to complete the extensive data already available on these solvents, while on silica gel separations and identification may be attempted. As shown in Fig. 1, perbromate moves faster than bromate and also faster than perchlorate and periodate on thin layers of silica gel.

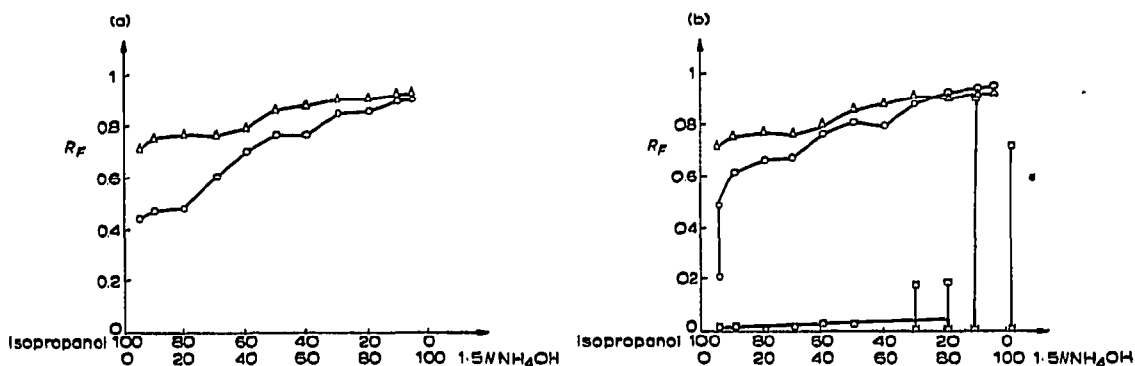


Fig. 1. R_F values of halo acids on Macherey-Nagel SIL G thin layers. Solvent: mixtures of isopropanol and 1.5 *N* ammonia solution. (a) R_F values of BrO_4^- (Δ) and BrO_3^- (\circ) plotted against the amount of 1.5 *N* ammonia solution in isopropanol; (b) R_F values of ClO_4^- (\circ), BrO_4^- (Δ) and IO_4^- (\square) plotted against the amount of 1.5 *N* ammonia solution in isopropanol.

ION-EXCHANGE CHROMATOGRAPHY

On anion-exchange resin paper, perbromate, perchlorate and periodate are strongly adsorbed and show only small differences in their R_F values. If one wants to establish the affinity sequence of these three ions on exchangers, equilibrium methods should not be used because reduction of perbromate to bromate can occur, which would affect the results.

TABLE V

R_F VALUES OF HALO ACIDS ON DEAE CELLULOSE THIN LAYERS

Thin layer: Macherey-Nagel Cell 300 DEAE. Eluent: aqueous sodium nitrate solution.

Ion	Concentration of NaNO_3 solution (<i>N</i>)			
	0.05	0.1	0.2	0.5
ClO_3^-	0.47	0.50	0.73	0.79
BrO_3^-	0.56	0.62	0.71	0.86
IO_3^-	0.58	0.63	0.76	0.85
ClO_4^-	0.37	0.41	0.56	0.66
BrO_4^-	0.31	0.37	0.43	0.62
IO_4^-	0 ↓ 0.58	0.60	0.73	0.81

It was noted¹, however, that the three perhalates were adsorbed less strongly on to a cellulose quaternary ammonium ion-exchange paper and that in this instance the sequence of adsorption was $\text{BrO}_4^- > \text{ClO}_4^- > \text{IO}_4^-$. We thought that more data on other anion exchangers would be needed in order to establish this sequence. Thin layers of diethylaminoethylcellulose (Macherey-Nagel Cell 300 DEAE) proved to be a suitable anion exchanger on which all of the halo acids moved as compact spots without reduction comets.

Table V and Fig. 2 show the results obtained, which confirm the above sequence on this exchanger. So far, the best separations of bromate and perbromate were obtained on thin layers of Cell 300 DEAE.

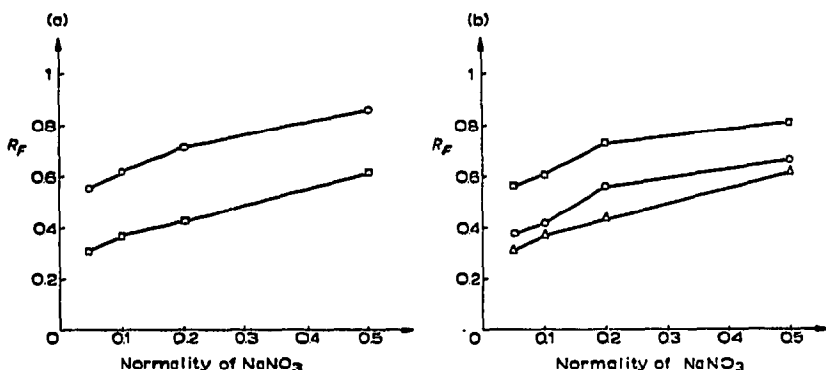


Fig. 2. R_F values of haloacids on Macherey-Nagel Cell 300 DEAE anion-exchange thin layers. (a) R_F values of BrO_4^- (\square) and BrO_3^- (\circ) plotted against the concentration of NaNO_3 used as eluent; (b) R_F values of ClO_4^- (\circ), BrO_4^- (\triangle) and IO_4^- (\square) plotted against the concentration of NaNO_3 used as eluent.

DISCUSSION

In this work, we have obtained further data on the behaviour of perbromate in solution in relation to perchlorate and periodate as well as in relation to chlorate, bromate and iodate. The following conclusions can now be drawn:

Perbromate reduces less readily than periodate but is less stable than perchlorate in spot test reactions.

In comparison with perchlorate, perbromate is better extracted by organic solvents in partition systems and more strongly adsorbed on anion exchangers. Periodate is treated here with some reservations because of its tendency to form acids of the type H_5IO_6 (however unlikely) and its tendency to form complexes with vicinal dihydroxyl groups and therefore also with cellulose.

While the sequence ClO_3^- , BrO_3^- , IO_3^- applies to ionic mobilities, partition and ion-exchange systems, BrO_4^- does not lie between IO_4^- and ClO_4^- in any of the partition and ion-exchange systems examined. Comparing only the pairs ClO_3^- - BrO_3^- and ClO_4^- - BrO_4^- , it is found that in partition systems chlorate moves faster than bromate while perchlorate moves slower than perbromate, and in ion-exchange systems the order is also reversed, chlorate moving slower than bromate and perchlorate moving faster than perbromate. Both are remarkable because chlorate and perchlorate have almost the same electrophoretic mobilities on paper in neutral NH_4NO_3 , and so have bromate and perbromate.

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