SEPARATION OF IODINE ANIONS BY GLASS FIBRE PAPER CHROMATOGRAPHY

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The study of isotope-exchange reaction kinetics can be made much easier by use of radiochromatography as demonstrated by MORÁVEK, NEJEDLÝ AND FILIP[1]. ARNIKAR AND TRIPATHI[2] used paper chromatography in their study of the iodide–iodate isotope exchange reaction. In connection with our experiments on isotope exchange between different oxidation states of iodine it was decided to use paper chromatography for the separation of the reaction products.

Several authors[3–8] have demonstrated the separation of the iodine anions I^-, IO_3^-, and IO_4^- on cellulose papers with various eluants. The purpose of this investigation was to study the method and to establish the best conditions for the separation.

Preliminary experiments with various cellulose papers and eluants invariably produced two spots for periodate. This phenomenon has also been reported by GRASSINI AND OSSICINI[5] for the system isopropanol–1.5 *F* ammonia, and by SERVIGNE[8] for the system isopropanol–water (3:1), but not for the many systems studied by other authors[3,4,6,7].

Since periodate is a strong oxidizing agent in both acid and alkaline medium and since it also forms complexes with polyhydroxy compounds such as cellulose, which are believed to be the first stage in the reduction of periodate, these multiple spots are to be expected. DOBICI AND GRASSINI[9] consider cellulose to be *a priori* unsatisfactory for trace-scale separations of periodate and iodate.

Glass fibre paper was then tried and produced satisfactory separations with several of the eluants tried. On account of the easy detection of small amounts, radioactive iodine compounds were used and the spots identified by their radioactivity as well as by chemical development. By comparison some separations were run on cellulose papers parallel to the separations on glass fibre paper.

EXPERIMENTAL

(a) *Synthesis of radioactive compounds*

Radioactive ^{131}I was delivered as essentially carrier-free sodium iodide in a dilute basic solution of sodium thiosulphate.

Potassium iodide. To a solution of 10 mg potassium iodide in 2 ml water 0.1 mC ^{131}I is added and the iodide is oxidized to iodine by adding 1 ml 6 *M* nitric acid and a few drops of 1 *M* sodium nitrite solution. The iodine is extracted into 2 ml carbon tetrachloride and back-extracted into water by shaking with 2 ml water containing a few drops of a 1 *M* solution of potassium bisulfite. The solution is acidified with 0.5 ml

of 6 *M* nitric acid, boiled to expel sulfur dioxide and subsequently made strongly basic (pH 14) with potassium hydroxide and diluted to 5 ml.

Potassium iodate and potassium periodate. These are prepared by a modification of WILLARD's method[10].

100 mg potassium iodide is dissolved in 3 ml water containing 1 mC ^{131}I, and 100 mg potassium chlorate is added to the resulting solution. The solution is warmed to boiling and made acid with 10 drops 6 *M* nitric acid. The reaction is finished when the iodine has completely disappeared. The resulting iodate solution is divided in two equal parts. One part is made basic with potassium hydroxide and diluted to 25 ml.

The other half is made basic with potassium hydroxide and 1 ml of a freshly prepared solution of 20% potassium hypochlorite is added. The solution is warmed to nearly boiling, and after 30 min heating, chlorine is passed in until all of the alkali is neutralized and insoluble potassium metaperiodate precipitates. The precipitate is centrifuged off and washed with cold water. In order to purify the preparation the metaperiodate is dissolved as soluble $K_4I_2O_9$ in 2 ml dilute potassium hydroxide solution, and subsequently the solution is neutralized with 6 *M* nitric acid which reprecipitates insoluble potassium metaperiodate. The precipitate is centrifuged off and washed with cold water. The dissolution, precipitation and washing is repeated twice more and leaves a product essentially free from other iodine compounds. Finally, the precipitate is dissolved in dilute potassium hydroxide solution and diluted to 25 ml.

In the following experiments aliquots of the three base solutions were measured with a NaI scintillation well counter, and larger portions were mixed to yield solutions with known specific activities of iodide, iodate and periodate.

(b) Chromatography and detection

The paper was cut in strips 40 cm by 3 cm and *ca.* 50 μl containing *ca.* 10 μg each of radioactive KI, KIO_3 and KIO_4 was applied as a thin line on to the paper. The papers were allowed to stand overnight to reach equilibrium with the saturated atmosphere in the jars. The elution was descending and the solvent front was allowed to advance *ca.* 25 cm before the elution was stopped. The radioactivity was measured by means of a radiochromatogram scanner coupled to a ratemeter and recorder. This allowed continuous scanning of the radioactive chromatograms. The recorder was set to the same speed as the scanner, usually 60 mm/h. To determine the total activity under the peaks, the spots were cut out of the paper and measured in the well counter. This allowed the calculation of the per cent recovery of the anions. Better than 95% recovery was obtained in all runs executed on glass fibre paper.

The chemical development of the spots was made according to FEIGL[11].

(1) *Iodide.* The paper is sprayed successively with a starch solution in 2 *M* acetic acid and a solution of 0.1 *M* potassium nitrite. A blue coloration indicates the presence of iodide.

(2) *Iodate.* The paper is sprayed successively with 2 *M* acetic acid and a solution of pyrogallol in acetone. A pink to brown spot indicates iodate. Periodate gives a similar colour.

(3) *Periodate.* Equal parts of a filtered solution of tetrabase (*p,p*-tetramethyldiamino-diphenylmethane) in 2 *M* acetic acid and a 10% solution of manganous chloride are mixed and sprayed on the paper. A blue coloration indicates periodate. Iodates and chlorates do not interfere with the test.

RESULTS

The R_F values obtained with Schleicher & Schüll glass fibre paper No. 6 are shown in Table I.

TABLE I

R_F VALUES OF I^-, IO_3^- AND IO_4^- ON GLASS FIBRE PAPER WITH VARIOUS SOLVENT SYSTEMS

No.	*Eluent composition*	*Reference*	*R_F values*		
			IO_4^-	*IO_3^-*	*I^-*
1	Ethanol–H_2O–15 F NH_3 (6:2:7)	4	0.01	0.84	0.93
2	Ethanol–H_2O–15 F NH_3 (12:2:7)		0.01	0.81	0.98
3	Ethanol–H_2O–15 F NH_3 (18:2:7)		0.01	0.54	0.95
4	Ethanol–H_2O–15 F NH_3 (24:2:7)		0.01	0.43	0.86
5	Ethanol–H_2O–15 F NH_3 (30:15:5)	3	0.00	0.70	0.97
6	Isopropanol–1.5 F NH_3 (7:3)	5	0.04	0.74	0.98
7	Butanol–1.5 F NH_3 (1:1)*		0.01	0.08	0.80
8	Butanol–ethanol–5 F NH_3 (1:1:1)		0.00	0.72	1.00
9	Butanol–ethanol–7.5 F NH_3 (2:1:1)		0.01	0.56	0.97
10	Acetone–1 F NH_3 (4:1)	6	0.01	0.46	0.96
11	Methyl isobutyl ketone–1.5 F NH_3 (1:1)*		0	0	0
12	Ethyl acetate–ethanol–1.5 F NH_3 (1:1:1)		0.01	0.82	0.98
13	Isopropanol–H_2O (3:1)	8	0.01	0.28	0.94
14	Butanol–acetone–H_2O (5:2:3)	6, 7	0.01	0.37	0.95

* Equal volumes were shaken. The organic phase was used for the elution, the water phase for saturating the chamber atmosphere.

The solvent fronts were somewhat indistinct and are best observed against a strong light. The positions of the spots were determined by measuring the distance from the starting line to the abscissa corresponding to maximum intensity of the recorded peaks. Nearly all the systems investigated produced essentially higher R_F values for iodate and periodate than reported for cellulose papers. The effect is particularly pronounced for the iodate and sometimes leads to an unsatisfactory separation between the iodate and iodide spots. This is the case for the systems ethanol–water–15 F NH_3 reported by LEDERER[3] and HALPERN[4]. An increase of the volume of ethanol in proportion to the volume of water and ammonia results in better separations, however, the iodate peaks are considerably broadened (see Fig. 1). Isopropanol–1.5 F NH_3 (7:3) produced very satisfactory separations. Acetone–1 F NH_3 (4:1) produced satisfactory R_F values, and the speed of elution is fast (25 cm in *ca.* 100 min) compared with the systems ethanol–water–15 F NH_3 (12:2:7) (25 cm in *ca.* 210 min) and isopropanol–1.5 F NH_3 (7:3) (25 cm in *ca.* 360 min). As a general rule a slow elution always seems to produce better defined spots than a fast one. The systems butanol–acetone–water (5:2:3)[6,7] and isopropanol–water (3:1)[8], are noteworthy because in some isotope exchange studies a strongly alkaline medium is contradicted in the subsequent separation of the exchanging species. Butanol–acetone–water (5:2:3) yields excellent separations on glass fibre paper.

It was never possible to detect any reduction products of periodate in the runs executed on glass fibre paper. Some runs were performed on cellulose papers parallel to

the separations on glass fibre paper. Whatman papers No. 1 and 2, and Schleicher & Schüll No. 2043 were tried. This always resulted in a reduction of the bulk of the periodate, probably to iodate, because the new spot always has almost the same R_F value as iodate and yields a positive test with pyrogallol and a negative test with tetrabase. Fig. 2 shows the results obtained when periodate is chromatographed on

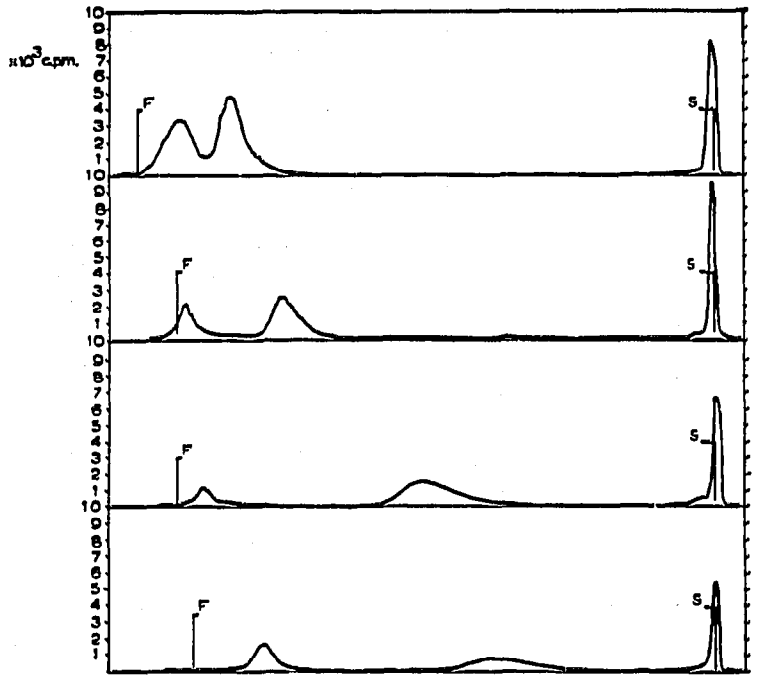

Fig. 1. Separation of iodide, iodate and periodate on Schleicher & Schüll glass fibre paper No. 6 with ethanol–water–15 F NH_3. From top to bottom: ethanol–water–15 F NH_3 (6:2:7); ethanol–water–15 F NH_3 (12:2:7); ethanol–water–15 F NH_3, (18:2:7); ethanol–water–15 F NH_3 (24:2:7). Scanning speed 60 mm/h; slit width 1.5 mm; time-constant ratemeter: RC = 45 sec. S = starting line; F = solvent front.

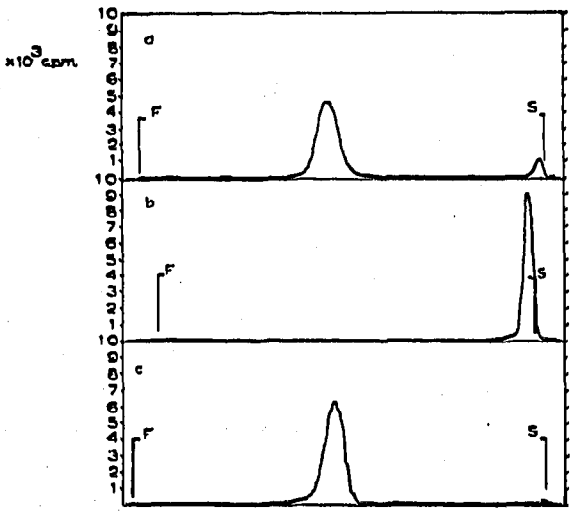

Fig. 2. (a) Periodate developed on Whatman cellulose paper No. 1. (b) Periodate developed on Schleicher & Schüll glass fibre paper No. 6. (c) Iodate developed on Whatman No. 1. Solvent: ethanol–water–15 F NH_3 (12:2:7). Scanning speed 60 mm/h; slit width 1.5 mm; time-constant ratemeter: RC = 45 sec; S = starting line; F = solvent front.

Whatman cellulose paper No. 1, and Schleicher & Schüll glass fibre paper No. 6 with ethanol–water–15 *F* NH_3 (12:2:7). For comparison a parallel run with iodate on Whatman No. 1 is included.

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SUMMARY

The separation of iodide, iodate and periodate by chromatography on glass fibre paper with different eluants is investigated. Cellulose papers are unsatisfactory for trace-scale separations of periodate because the bulk of the periodate is reduced, probably to iodate.

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