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PAPER CHROMATOGRAPHIC STUDY OF THE REDUCTION OF PERBROMATE IONS BY POTASSIUM AND HYDROGEN HALIDES

S. K. SHUKLA*, S. FANALI and L. OSSICINI
Laboratorio di Cromatografia del C.N.R., Via Romagnosi 18A, Rome (Italy)
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SUMMARY

The reduction of perbromate ions by potassium and hydrogen halides has been studied by paper chromatography. Chloride ions (only as derived from Merck fuming hydrochloric acid) reduce perbromate ions very slowly to bromide ions. Potassium bromide and potassium iodide reduce perbromate ions to bromate in aqueous systems while the reduction is more rapid and proceeds to bromine in acidic solution. Hydrobromic and hydriodic acids at all concentrations reduce perbromate ions.

INTRODUCTION

In spite of the high potential of the perbromate–bromate couple (+1.74 V in acidic solution[1–5] and +0.93 V in basic solution[5]), perbromate ions are known to act as a sluggish oxidising agent of low reactivity[4,6]. At 100°, 6 *M* perbromic acid is a powerful oxidising agent, while the 12 *M* acid acts as a vigorous oxidant at room temperature[6]. Perbromic acid at concentrations greater than 6 *M* is unstable and decomposes to bromine and oxygen[4,6]. Perbromate ions have been found[6] to be reduced to Br_3^- by 12 *M* hydrobromic acid. This reaction has been used for the titrimetric determination of perbromate ions[6,7].

The reduction of perbromate ions by iodide ions has already been reported[6,8–10] and studied chromatographically[10].

In this paper, we describe the results obtained in the paper chromatographic analysis of the reaction mixture involved in the reduction of perbromate ions by aqueous and acidic solutions of potassium halides and by the halogen acids alone.

EXPERIMENTAL

Potassium perbromate was generously supplied by Dr. E. H. Appelman and the Argonne National Laboratory. The concentration of perbromate solution was kept at 5.5×10^{-3} *M* throughout. Other reagents were of analytical grade. Fuming hydrochloric acid (Merck, Darmstadt, G.F.R.) had a minimum concentration of 37%.

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* Present address: Laboratorio de Chimica Nucleare del C.N.R., Montelibretti, Casella Postale 10, Monterotondo Stazione, Rome, Italy.

Chromatographic analysis of the reaction mixture was carried out on acid-washed Whatman 3MM paper strips (20 × 3 cm, with a chromatographic run of 15 cm), using 98.5 % (v/v) aqueous methanol as the mobile phase. A typical chromatogram showing the separation of the different oxidation states of bromine present in a solution is shown in Fig. 1. This system has been found[11] to be the most suitable with regard to both its capacity to separate all of the stable oxidation states of bromine and the speed of development of the chromatogram.

A ratio recording spectrophotometer (Beckmann DK 2A) was used for spectral analysis of the reaction solution in 1-cm quartz cells.

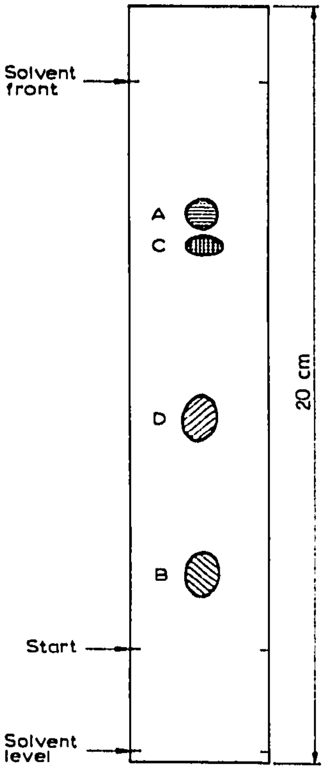

Fig. 1. Chromatographic separation of (A) perbromate, (B) bromate, (C) bromine + hypobromite and (D) bromide ions on Whatman 3MM paper strips with 98.5 % aqueous methanol as solvent at 20 ± 1.0°.

RESULTS AND DISCUSSION

Reduction of perbromate ions in chloride systems

It was found that concentrated hydrochloric acid (37 %, Carlo Erba, Milan, Italy) and saturated potassium chloride solution did not reduce perbromate ions, as indicated by the absence of colour, there being always a single spot with an R_F value corresponding to that of the fresh solution of perbromate, and no modification of the spectrum of the reaction mixture on ageing (even after 353 days). Fuming hydrochloric acid (37% minimum, Merck), on the other hand, reduced perbromate ions very slowly at room temperature. A light green-yellow coloration developed in the reaction mixture after ageing for about 1 week. Chromatographic analysis of this coloured solution showed the presence of perbromate ions only, but with reduced intensity. These observations lead to the conclusion that the fuming hydrochloric acid reduces perbromate ions directly to bromide ions.

The absorption spectrum of the fresh solution had a maximum at 215 nm and a barely visible shoulder at 225 nm. Appelman[6] observed a shoulder at 215 nm in an aqueous solution of potassium perbromate. On ageing the solution for only 5 h, the shoulder at 225 nm increased in intensity and was not measurable after 6 h. A new band appeared at 337.5 nm. A blank test of the spectrum of a solution of chlorine in the fuming hydrochloric acid showed that the maximum at 337.5 nm is due to the chlorine liberated when perbromate ions oxidise hydrochloric acid. On ageing the solution for 41 days, the maximum at 337.5 nm increased to the full scale, while the maxima at lower wavelengths passed beyond the scale. Chromatographic analysis of this solution also did not show the presence of any species other than perbromate ions. This result is in agreement with the previous finding[12,13] that bromate ions oxidise hydrochloric acid to free chlorine.

Reduction of perbromate ions in bromide systems

As already mentioned, 12 *M* hydrobromic acid reduces perbromate ions to Br_3^- at room temperature. The rate of oxidation of perbromate depends on the concentration of perbromate ions in the solution[6]. It was therefore of interest to examine the behaviour of perbromate ions with hydrobromic acid of lower concentrations.

Hydrobromic acid concentrations of 8.8, 4.4 and 1.0 *M* were used. As with the 12 *M* acid, hydrobromic acid at lower concentrations also reduces perbromate ions directly to Br_3^-, as shown by the brown coloration of bromine in the solution and a band in the chromatogram representing bromine. Hydrobromic acid at concentrations of 8.8 and 4.4 *M* requires 8 and about 150 min, respectively, for the completion of the reduction. Hydrobromic acid of 1 *M* concentration reduces perbromate ions very slowly, and only after 24 h could a yellow tinge due to bromine be observed. On ageing the solution for 13 months, a small amount of perbromate ions still remained. An excess of potassium bromide caused a more rapid reduction, complete reduction taking about 24 h. On heating on a boiling water-bath, it took 4 h for the perbromate ions to be completely reduced. Here also, although bromate ions react readily with hydrobromic acid to give free bromine[14,15], the presence of the latter, if produced as an intermediate in the reduction, could not be observed by chromatography.

An aqueous solution of potassium bromide reduces perbromate ions to bromate ions. In the reaction mixture before the completion of the reduction, the presence of both perbromate and bromate ions was found on the chromatogram. As the reduction progressed, the perbromate spot became weaker in intensity and the bromate spot became more and more intense. Further ageing or heating of the reaction mixture on a boiling water-bath did not produce any change in the bromate spot on the chromatogram and the reaction mixture remained colourless. The reduction was studied in saturated 4 *M* and 1 *M* potassium bromide solutions. The speed of reduction depended on the potassium bromide concentration and on the temperature. It was necessary to age a saturated solution of potassium bromide for 1 week for the conversion of perbromate to bromate ions to be complete, while the other two solutions showed the presence of perbromate ions on the chromatogram even after ageing for 2 months.

The reason for the two types of reduction by bromide ions, depending on whether the reduction is carried out in a neutral aqueous system (when bromate is the final product) or in an acidic system (when bromine is the final product), lies in the reduction potential of the bromate–bromide couple in the two media[16], which is only +0.61 V in an aqueous system compared with +1.44 V in an acidic system[5].

Reduction of perbromate ions in iodide systems

The reduction of perbromate ions in 4.4 and 1.0 *M* potassium iodide solutions was examined chromatographically. As in the bromide system, reduction to bromate ions takes place. The speed of reduction in this instance also depends on the concentration of potassium iodide and on the temperature. Potassium iodide of concentration 4.4 *M* reduced perbromate ions after ageing the solution for about 4 days, while a 1.0 *M* solution required 2 weeks before a solution free from perbromate ions was obtained. Heating on a boiling water-bath for 5 hours was sufficient for complete reduction of the perbromate ions to occur in the latter instance.

Hydriodic acid at all concentrations reduced perbromate ions immediately to bromide ions at room temperature, as indicated by the absence of spots representing perbromate, bromate and bromine + hypobromite ions on the chromatogram of the fresh solution.

The reduction of perbromate ions in mixtures of potassium iodide and hydrochloric acid has been studied chromatographically[10] in sodium nitrate as a mobile phase. A complex chromatographic pattern was found, the species in which could not be identified. A chromatographic study of this system followed by the present solvent system may give further information about the reduction path and the reaction products.

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