

THE APPLICATION OF PAPER ELECTROPHORESIS TO THE SEPARATION OF RADIOACTIVE PRODUCTS FOUND IN THE SZILARD-CHALMERS REACTION*

J. JACH, H. KAWAHARA** AND G. HARBOTTLE

Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, N.Y. (U.S.A.)

INTRODUCTION

When the nucleus of an atom captures a thermal neutron and, in de-excitation, emits gamma rays, the atom involved suffers a sharp recoil, the energy of recoil typically amounting to a few hundred electron volts. Since chemical bond energies are only of the order of a few electron volts, it follows that the recoil atom will generally break free of its original molecular combination. This energetic atom will then be slowed down by collisions with neighboring atoms and finally come to rest at thermal energies.

It has been frequently observed that the recoil atom can engage in chemical reactions during or after its slowing-down, such that one finally obtains the radioactivity distributed among a number of chemically separable species¹. For example, if one studies the distribution of radioactive bromine in neutron-irradiated normal propyl bromide (liquid or solid), one finds bromine activity in the form of both normal and isopropyl bromide, in ethyl and methyl bromide and even in methylene bromide upon fractionation². These chemical effects of nuclear transformation are generally referred to as SZILARD-CHALMERS reactions, after the discoverers³.

We have been interested in SZILARD-CHALMERS reactions in crystalline inorganic substances, and have found that the method of paper electrophoresis provides a valuable tool for the separation and quantitative estimation of the various chemical species synthesized by the nuclear recoil process. The use of paper electrophoresis for this purpose was first suggested by CROATTO, GIACOMELLO AND MADDOCK⁴ who employed it in the analysis of irradiated sodium chloridate. For studies of this type we believe that paper electrophoresis offers several outstanding advantages over ordinary wet-chemistry separations. (1) Quantitative estimations of the various radioactive fractions are easily obtained by merely summing the counting rates under the different peaks. Furthermore, one can be certain that account is taken of all the radioactivity in the solution as there are no losses due to adsorption on the walls of vessels, incomplete phase separation in extraction techniques, incomplete precipitation, etc. (2) The method gives an unequivocal determination of the sign of charge of an unknown species. (3) Electrophoresis on paper is remarkably sensitive

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** Guest Research Collaborator from the Chemistry Laboratory, Otaru College of Commerce, Otaru, Japan.

in separating species which are weakly radioactive (*i.e.* present in only small yield) from other species which carry the bulk of the radioactivity. Thus one can separate, and accurately estimate, species carrying $\sim 1\%$ or less of the total radioactivity without danger of cross-contamination. (4) One may help confirm the identification of unknown species by comparing their migration rates with those of known specimens. (5) The position of the parent species may usually be established by chemical tests, since in a SZILARD-CHALMERS study it is the only species present in macroscopic quantities.

EQUIPMENT

The paper-electrophoresis apparatus consisted of two glass plates 45 cm square resting on tanks which were ordinary Pyrex oven casseroles. The surfaces of the plates touching the paper were treated with "Drifilm" to prevent wetting. Provision was made for cooling the upper plate with water when necessary. Strips of Whatman 3 MM paper were cut 55 cm long by either 3.8 or 1 cm wide; these strips were ruled off in centimeters and were trimmed, at the ends, into "tails" about 2 mm wide which dipped into the tanks. The purpose of this was to prevent excessive entry of electrolyte from the tanks into the ends of the paper, while maintaining electrical contact. Before use these papers were soaked for a few seconds in the electrolyte solution desired and firmly blotted for *ca.* 3 minutes between sheets of absorbent "Kimpak". The solution of irradiated crystals to be examined was then placed at the zero-line on the paper by means of a lambda-pipette: volumes of 3 to 10 λ were generally employed. The paper was firmly clamped between glass plates, and electrical contact was made through graphite electrodes dipping in the electrolyte tanks. Potentials of 450-700 V D.C. were applied (10-16 V/cm gradient). The entire high-voltage end of the apparatus was surrounded by a plastic shield to prevent accidental contact and electrical injury to personnel. Currents were usually a few milliamps, which did not generally cause serious heating of the paper.

After 2-5 hours the voltage was cut off, the apparatus disassembled and the paper dried by a current of warm air from a hair-dryer. When dry the paper was cut into sections 1 cm long which were counted in reproducible geometry with an end window proportional counter, if beta radioactivity was determined, or a scintillation counter for gamma radiation. The radiation characteristics and rate of decay of individual fractions could be easily checked to confirm the identity of the radioactivity present at various points along the paper.

EXPERIMENTAL RESULTS

(a) Alkali bromates

It is well-known that when crystalline alkali bromates are irradiated, radioactive bromine is found in both the bromate and bromide form⁵. The percentage found as bromate is usually $\sim 10\%$ ⁶. When irradiated alkali bromates were dissolved in 0.1 N NaOH and subjected to electrophoresis on paper saturated with 0.01 N NaOH,

histograms similar to Fig. 1 were obtained. In this plot, as in all others in this paper, the ions start from the dashed vertical line and anions move to the right. The peak farthest to the right is bromide, the adjacent one being bromate. Two other, very

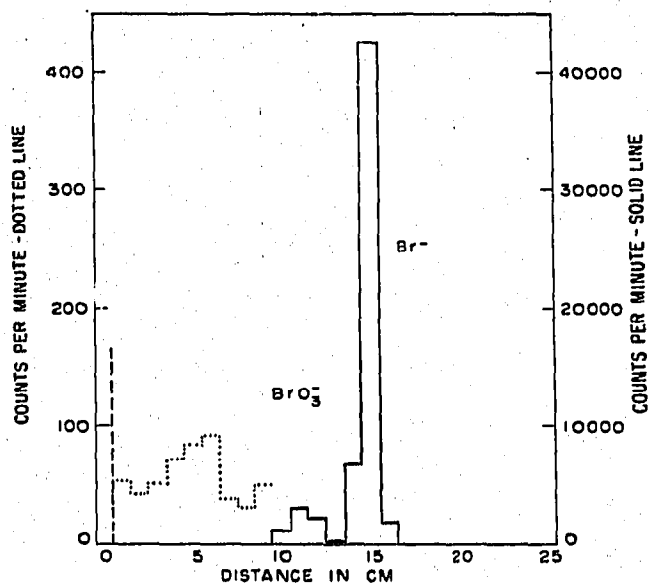


Fig. 1

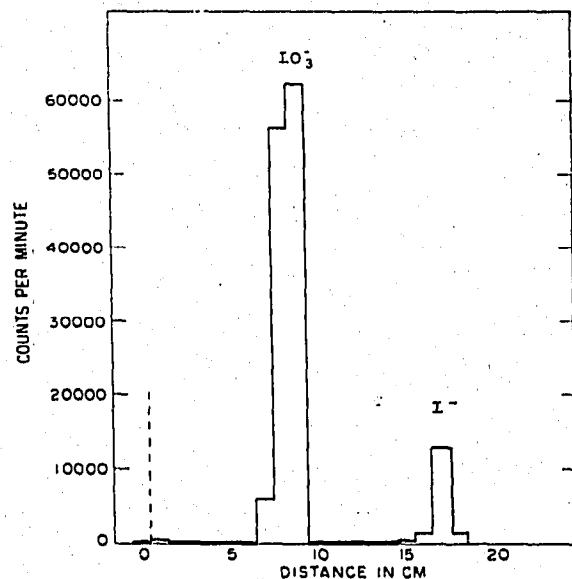


Fig. 2

Fig. 1. CsBrO_3 irradiated with neutrons and dissolved in 0.1 *N* NaOH. Paper wet with 0.01 *N* NaOH. Running time 1.5 h at 600 V.

Fig. 2. KIO_3 irradiated with neutrons and dissolved in 0.1 *N* NaOH. Paper wet with 0.01 *N* NaOH. Running time ca. 1.5 h at 600 V.

much smaller, peaks were observed: these appear in the histogram as the dotted curve, whose ordinates are given on a separate scale. The small peak at the origin is probably formed by an irreversible reaction of some component in the solution with the paper, but the identity of the small peak at 5–6 cm could not be established. It is an anionic species and was shown to contain bromine by analysis of its radiation characteristics. The small peak was shown not to be hypobromite by its continued appearance even when sulfite was added to the dissolution medium. It is likely that a conventional chemical analysis would not have detected this component.

The electrophoresis method also effects a separation of the bromine anions from radioactive cations (sodium, potassium, rubidium and cesium) simultaneously formed during neutron irradiation as these species move in the opposite direction and are eliminated.

The relative rates of motion of bromide and bromate ions in paper electrophoresis have been previously reported by GROSS⁷ and LEDERER⁸ in ammonium carbonate solutions. They find that the ratio of the velocity of bromide to that of bromate is 1.41 and 1.24 respectively. We obtain, for 0.01 *N* NaOH, a ratio of 1.26.

(b) Potassium iodate and periodate

When crystalline potassium iodate is irradiated with neutrons most of the radioactive iodine is found after dissolution in water in the form of iodate and iodide, with no

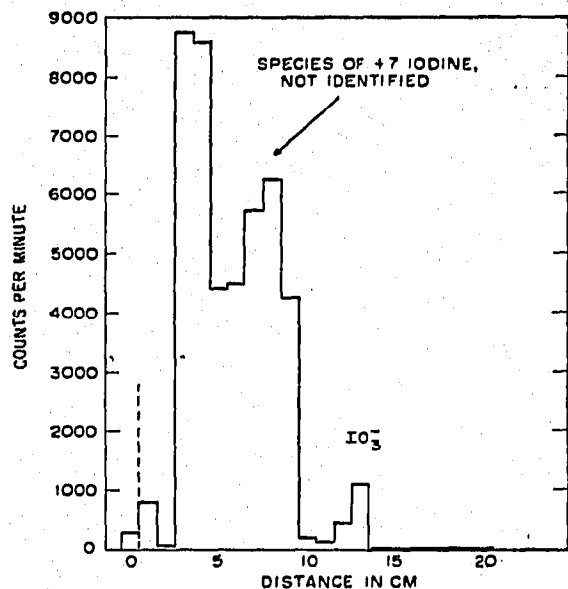


Fig. 3

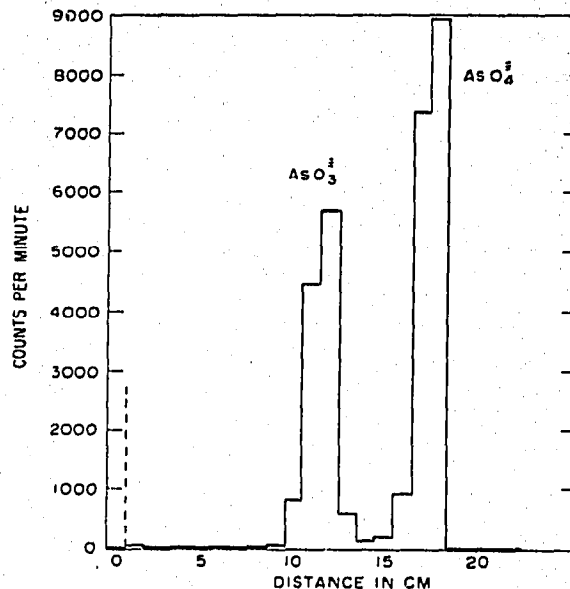


Fig. 4

Fig. 3. KIO_4 irradiated with neutrons, annealed at 240° for 15 min, and dissolved in 0.1 N NaOH. Paper wet with 0.01 N NaOH. Running time 2 h at 600 V.

Fig. 4. As_2O_5 irradiated with neutrons and dissolved in 0.1 N NaOH. Paper wet with 0.01 N NaOH. Running time 2 h at 600 V.

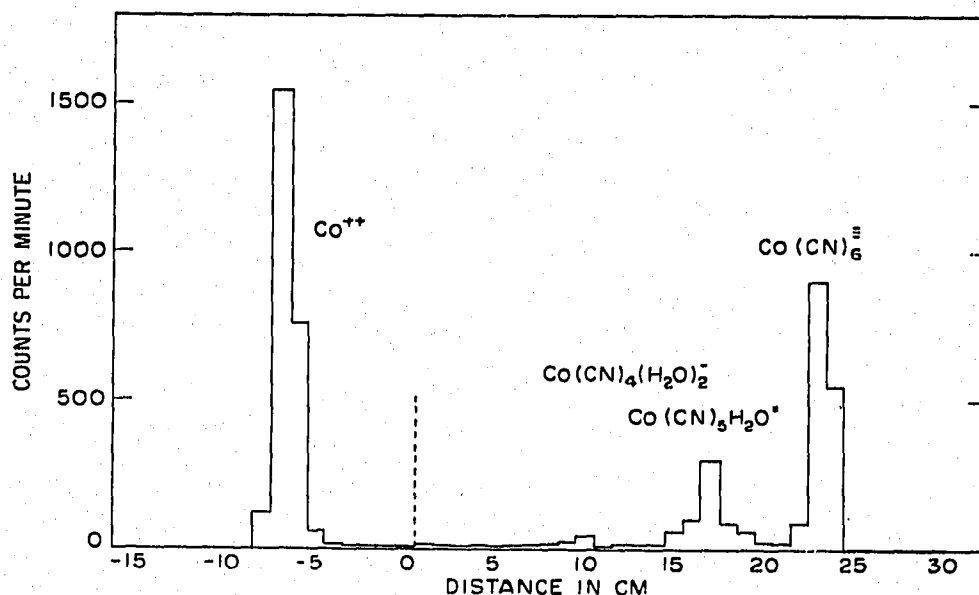


Fig. 5. $\text{K}_3\text{Co}(\text{CN})_6$ irradiated with neutrons and dissolved in pH 5.4 buffer. Paper wet with pH 5.4 buffer. Running time ca. 3 h at 600 V.

detectable periodate⁹. Under the same conditions as for bromate above, we obtained histograms of which Fig. 2 is a typical example. The iodate and iodide peaks are seen to be clearly resolved. There is no evidence of a large periodate peak in this histogram, in agreement with other methods of analysis.

In the case of potassium periodate, ATEN *et al.*¹⁰ have shown that the neutron irradiation produces about 10% I^- , 86% IO_3^- and 4% IO_4^- . However, they found

that when the irradiated crystals were annealed at temperatures $\sim 100^\circ$ the species which produce I^- on dissolution passed over into species producing IO_3^- while at higher temperatures the IO_3^- began to go over to IO_4^- . Under annealing at 240° for 15 minutes they found no iodide, $\sim 80\%$ IO_4^- and $\sim 20\%$ IO_3^- . Since we wished to observe the electrophoresis behavior of IO_4^- we irradiated a sample with neutrons and annealed it for 15 minutes at 240° . A typical histogram obtained under these conditions is shown in Fig. 3; this experiment was repeated several times. The individual fractions on the paper were chemically tested for the presence of periodate by spotting with an acidic starch-iodide solution. A blue color developed for fractions lying at 9 cm and lower, but not for the peak at 12-13 cm, showing that this peak is not periodate but that the large twin peaks at 3-4 cm and 7-8 cm are both species of +7 iodine, as well as the peak at the origin. Had iodide been present, it would have appeared at strip 17 or beyond. Evidently, the separate peaks of +7 iodine represent different ionic forms not in rapid equilibrium with one another in dilute base. These species may be IO_4^- and related ions, as for example species arising from

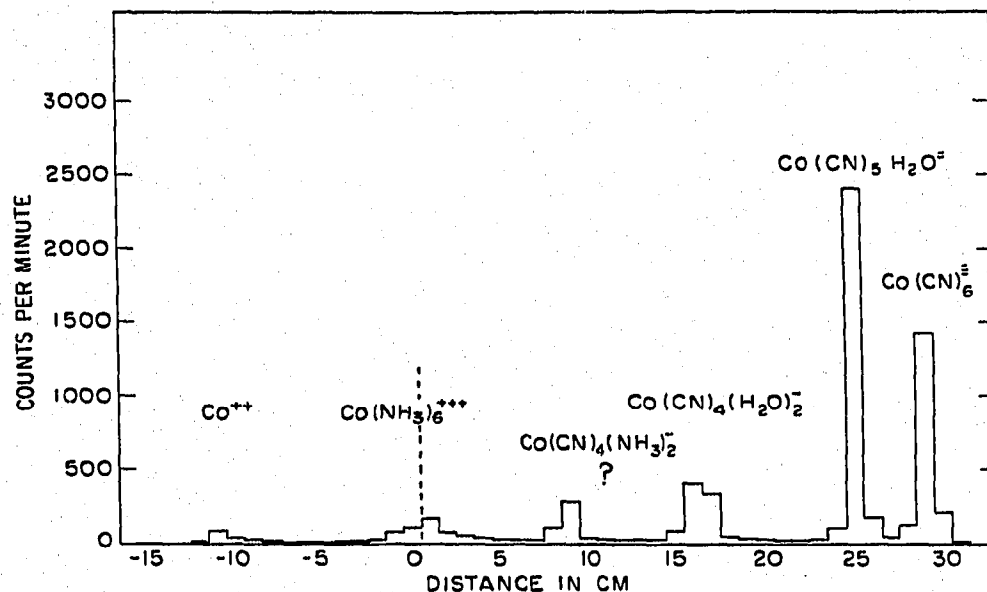


Fig. 6. $K_3Co(CN)_6$ irradiated with neutrons and dissolved in conc. NH_4OH . Paper wet with pH 5.4 buffer. Running time ca. 4 h at 600-650 V.

the acids H_5IO_6 or $H_4I_2O_9$, which have been reported in the literature¹¹.

The sequence of velocities for paper electrophoresis in a basic medium, $I^- > IO_3^- > IO_4^-$ has been previously reported by GROSS⁷ who studied iodide and iodate, and LEDERER⁸, who reported on all three. LEDERER also found that periodate gives two spots and a "reduction comet". We do not observe reduction on Whatman 3 MM paper wet with 0.01 N NaOH and seem to find three spots: it is possible however that one of these may be a spurious "stain" due to irreversible reaction with the paper at the starting line.

(c) *Arsenite-arsenate*

We have also employed paper electrophoresis to separate tri- and quinquevalent

arsenic formed by neutron capture in As_2O_5 (solid). A typical histogram is presented in Fig. 4: here the neutron-irradiated As_2O_5 was dissolved in 0.1 *N* NaOH and the paper was soaked in 0.01 *N* NaOH. LEDERER⁸ has also given data on arsenate and arsenite in basic solution. He finds that (in 2% ammonium carbonate) the ratio of velocities of arsenate to arsenite is 1.67. We find a ratio of 1.54. Our data (Fig. 4) also indicate the production of a small quantity of elementary arsenic, which remains at the origin.

(d) *Potassium cobalticyanide*

A study of the recoil reactions of cobalt in potassium cobalticyanide has recently been completed in this laboratory¹². The paper electrophoresis method was used to separate the complex ionic species containing cobalt from one another and from cobaltous ion. The first histogram (Fig. 5) shows the distribution of cobalt activity when the neutron-irradiated salt was dissolved in pH 5.4 buffer: in this plot are seen peaks corresponding to cobaltous ion (in the cation direction) and to several anionic species formed by reaction of partially-stripped radioactive cobalt-cyanide fragments with water. The second histogram (Fig. 6) shows the distribution when the same material was dissolved in concentrated ammonia: the paper was again wet with

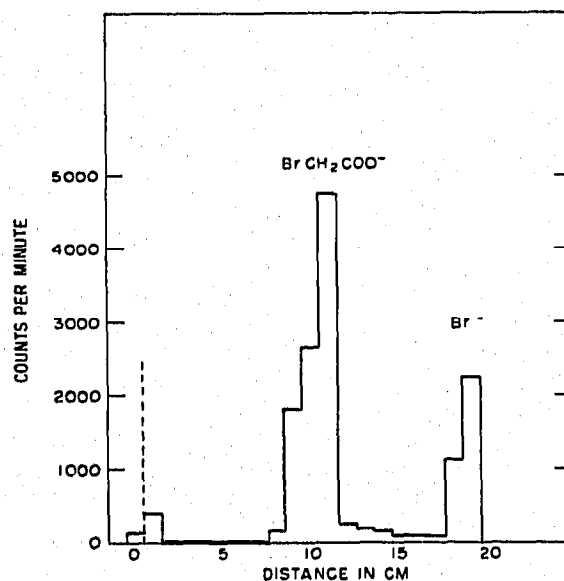


Fig. 7. BrCH_2COOH irradiated with neutrons and dissolved in 0.1 *N* NaOH. Paper wet with 0.01 *N* NaOH. Running time ca. 1.5 h at 600 V.

pH 5.4 buffer. Here two new peaks have appeared, at ~ 9 cm and at the origin. The peak at the origin is $\text{Co}(\text{NH}_3)_6^{+++}$ formed by the air-oxidation of Co^{++} in ammoniacal solution. The peak at ~ 9 cm is a species whose identity it was not possible to establish definitely, but is probably a mixed cyano-ammino cobaltate such as $\text{Co}(\text{NH}_3)_2(\text{CN})_4^-$.

These examples demonstrate an application of paper electrophoresis which has already been exploited by several workers^{13, 14, 15}, namely, the separation and iden-

tification of complex ions of the transition groups, in connection with analytical, synthetic or kinetic studies.

(e) *Bromacetate-bromide*

In these experiments bromacetic acid was irradiated with neutrons and dissolved in 0.1 N NaOH. A typical histogram, showing the separation of bromacetate and bromide ions, is shown in Fig. 7.

SUMMARY

It has been shown by these examples that the technique of paper electrophoresis, using inexpensive equipment which can be put together in almost any laboratory, is capable of separating many of the radioactive ionic species formed in typical SZILARD-CHALMERS reactions, and is also useful in assisting in their identification.

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