

THE ISOTOPE EXCHANGE REACTION BETWEEN IODIDE AND IODATE IONS STUDIED BY CHROMATOGRAPHY

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PESCHANSKI¹ used elution chromatography on a column of alumina for studying the Fe(II)–Fe(III) and Hg(I)–Hg(II) isotope exchange reactions under conditions where the reactions proceeded to completion immediately on mixing. She also employed paper chromatography, with and without electrophoresis, under conditions where the reaction was either wholly or partly completed *before* chromatography. In the last case allowance had to be made for the amount of change taking place *during* chromatography, when the reactants were in contact but with a progressively changing relative concentration. The method would appear, therefore, to be inapplicable for studying the kinetics of the exchange in cases where separation-induced exchange is involved.

This limitation does not arise when the reaction takes place at a sufficiently high temperature and is effectively quenched at room temperature, at which chromatography is usually conducted. The kinetics of the reactions $S^*O_3^{2-}-S_2O_3^{2-}$ and $S^*O_3^{2-}-C_6H_5CH_2S_2O_3^-$ were studied in these laboratories in the temperature range 40–90°, utilizing paper chromatography for analysing the reaction products^{2,3}.

The isotope exchange between I^{*-} and IO_3^- especially in a neutral medium, is a high temperature reaction not conveniently measurable even at 50°, where the period of half-exchange is reported to be longer than 30 years⁴. Following negative results of earlier workers^{5,6}, ZABORENKO, NEĪMAN AND SAMSONOVA⁷ were the first to report kinetic data for this exchange reaction in the temperature range 100°–300°. The analogous exchange reaction between I_2 and IO_3^- was studied by MYERS AND KENNEDY⁴.

The complete quenching of the reaction at room temperature and the extreme ease with which the I^- and IO_3^- ions can be separated by paper chromatography, seem to make it ideally suited to be studied by this method, which requires only a very small amount of the reaction mixture for each analysis. The results of our work reported below bear out this expectation.

EXPERIMENTAL

A series of preliminary experiments showed that a mixture of acetone and 1 *N* NH_4OH (4:1), as recommended by YAMAGUCHI⁸, was most suitable for a separation

of I⁻ and IO₃⁻ ions by paper chromatography, the R_F values being 0.81 and 0.07 respectively. A complete separation of the two reactant species is, therefore, easily effected.

The exchange reaction I^{*}-IO₃⁻ was studied for three different equilibrium concentrations of the reactants: (a) 0.005 M KI + 0.005 M KIO₃; (b) 0.005 M KI + 0.05 M KIO₃; and (c) 0.055 M KI + 0.075 M KIO₃. In all experiments, the iodide solution was labelled with ¹³¹I, supplied in a carrier-free state by the Atomic Energy Establishment, Trombay. After labelling, the specific activity of the iodide solution was determined in each case. Six to eight samples of 1 ml of each reaction mixture were hermetically sealed in pyrex tubes and kept in an electric muffle at a temperature of 240° ± 5°. Each sample was taken out of the muffle after a definite time interval and chilled to room temperature. Then 0.005 ml was withdrawn, spotted on strips of 30 × 2 cm of Whatman No. 1 paper and chromatographed with the above-mentioned solvent, ascending development being employed. When the solvent front had mounted 12 cm, the paper was taken out, quickly dried and cut into samples of 5 mm length. The radioactivity (*a*) of each sample was measured under conditions of constant geometry using a shielded G.M. Counter. Fig. 1 is a

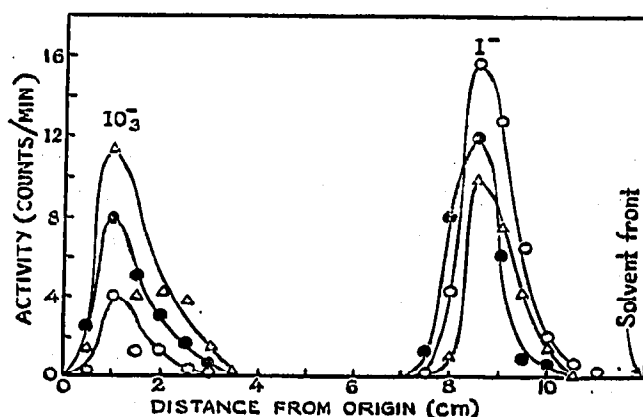


Fig. 1. Chromatogram showing the distribution of ¹³¹I between I⁻ and IO₃⁻ in the isotope exchange reaction at 240° for the reactant concentrations [I⁻] = 0.055 M and [IO₃⁻] = 0.075 M. Time: ○—○ 2 h; ●—● 4 h; △—△ 6 h.

typical example of the distribution of the activity as a function of the distance from the origin. It can be seen that the two peaks corresponding to I⁻ and IO₃⁻ are sharp and well separated by a blank zone of about 2 cm. From this chromatogram the distribution of ¹³¹I between IO₃⁻ and I⁻, at the end of a certain time, was determined in each case by measuring the area under the corresponding peak. This is represented by the ratio

$$a_{\text{IO}_3^-} / a_{\text{I}^-}.$$

The reaction velocity, R , can easily be determined with the MCKAY relation⁹,

$$Rt = \frac{2.303 [\text{I}^-] [\text{IO}_3^-]}{[\text{I}^-] + [\text{IO}_3^-]} \log (1 - F)$$

where the quantities in brackets are the equilibrium concentrations of iodide and iodate in moles per litre. F is the ratio of the radioactivity in the iodate species attained at time t to that at equilibrium, and is given by:

$$F = (a_{\text{IO}_3^-})_t / (a_{\text{IO}_3^-})_{\text{equil.}}$$

From the slope of the linear plot of $\log(1 - F)$ vs. t (Fig. 2). R can easily be determined. The period of half-exchange, $t_{1/2}$, can be calculated from the above relation by putting $F = 0.5$, viz.:

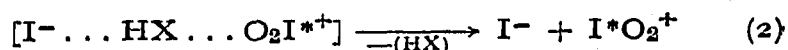
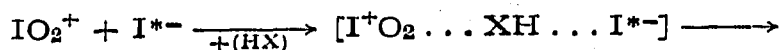
$$t_{1/2} = \frac{[\text{I}^-][\text{IO}_3^-]}{[\text{I}^-] + [\text{IO}_3^-]} \frac{0.693}{R}$$

A typical set of results is given in Table I.

TABLE I

| $[\text{I}^-]$ (moles/l) | $[\text{IO}_3^-]$ (moles/l) | $R \times 10^4$ (moles $l^{-1} h^{-1}$) | $t_{1/2}$ (h) | Induction period (h) |
|-----------------------------|--------------------------------|---------------------------------------------|------------------|-------------------------|
| 0.005 | 0.005 | 3.8 | 4.8 | 5.8 |
| 0.005 | 0.05 | 13.5 | 2.3 | 4.0 |
| 0.055 | 0.075 | 173.8 | 1.3 | 1.5 |

The above results agree with the general first order reversible reaction for the exchange rate. The actual mechanism is, however, complex and comprises the essential steps:



Of these, reactions (1) and the reaction (3), are fast and reversible, while (2), involving the transfer of two electrons between the iodine species, is considered as the rate determining step. This last step is facilitated in an acid (HX) medium.

Our results (Fig. 2) indicate the existence of an induction period in the iodide-iodate exchange reaction of the order of 1-6 hours, depending on the concentrations of the reactants; this period is possibly associated with the formation of iodine (and free acid) in traces, essential for the initiation of the series of reactions envisaged in the exchange mechanism. In all probability I^- - IO_3^- exchange does not occur in a purely neutral medium of iodide and iodate, as has been reported^{5,6,10}.

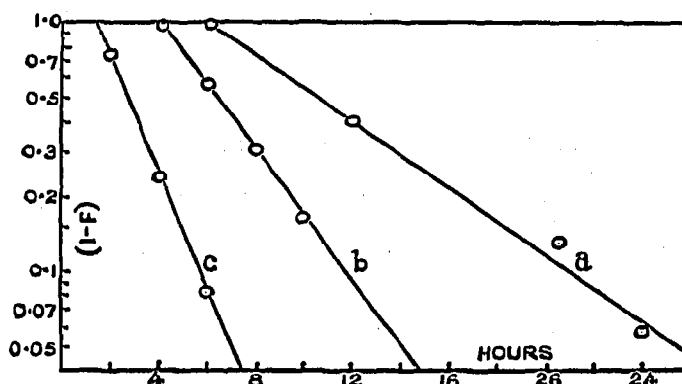


Fig. 2. Relationship between isotope exchange ratio and time, at 240° for reactant concentrations: (a) $0.005 M KI + 0.005 M KIO_3$; (b) $0.005 M KI + 0.05 M KIO_3$; (c) $0.055 M KI + 0.075 M KIO_3$.

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SUMMARY

It is shown that paper chromatography can conveniently be employed for studying the high temperature isotope exchange reaction between iodide and iodate ions. By means of this method the reaction velocity and period of half-exchange were calculated for the reaction at 240° for three different equilibrium concentrations of the reactants. The data indicate the existence of an initial induction period, which is probably associated with the formation of traces of iodine and free acid, the iodide-iodate isotope exchange being considered as non-existent when the pure reactants are present in a neutral medium.

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