

Radioactive Isotope Tracer Study of the Kinetics of Anion Exchanger Thermax A-127

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ABSTRACT

The kinetics of the ion exchange reaction $R I + I^{*} = R I^{*} + I^{-}$ in the strongly basic anion exchanger Thermax A-127 has been studied using isotope tracer technique. The specific reaction rate at 25°C and energy of activation are found to be 0.156 min⁻¹ and 14.7 KJ mole⁻¹ respectively. The rate of ion exchange is observed to vary linearly with the square root of the iodide ion concentration. The results are confirmed by considering the ion exchange reaction, under study, as an isotope exchange reaction.

Keywords: Isotope tracer, kinetics of anion exchanger, Thermax A-127

INTRODUCTION

Majority of the study, regarding the kinetics of ion exchange reactions deals with the exchange of the unlike ions¹⁻⁴. It would be of great interest to study isotopic exchange of the same ions to know the intrinsic rate of ion exchange and which would be a characteristic of the ion in the resin. Such types of studies are very scanty⁵⁻¹⁰ and hence present investigation has been undertaken. The rate of exchange between radioactive iodide ions (I¹³¹) in the solution and the iodide ion from resin has been studied. The effect of iodide ion concentration as well as amount of resin on the rate of exchange has been investigated. Keeping in view the particular ion exchange reactions under study, the results have also been pondered from the viewpoint of isotope exchange.

Material & Methods:

The kinetic studies are carried out with Thermax A-127. This is a strongly basic anion exchanger containing the quaternary ammonium group. It is in the form of uniform sized spherical beads of 15-100 mesh size. The resin is supplied in the chloride form and for the present study it is converted into the iodide form¹¹. The kinetics of ion exchange is carried out in two parts.

Effect of iodide ion concentration: 200 cm³ of 0.005M potassium iodide solution was labeled with a few microliters of a solution of radioactive iodide in such a way that one cm³ of the solution has an activity of about 16000 counts per minute when measured with gamma ray spectrometer. The solution was maintained at 25°C in thermostat and one gram of resin was quickly transferred into the solution keeping the later vigorously stirred. Simultaneously a stopwatch was started. After every two minutes, one cm³ of the solution was pipetted out into dry test tube and its radioactivity was measured. The solution was transferred back and after half an hour pipetting out was done at longer intervals. The experiment was continued about four hours.

The activities measured were corrected for background counts and radioactive decay. Preliminary studies showed that the reaction is of first order. The logarithm of corrected activity versus time yields a composite curve in which the activity initially decreases sharply but later, very slowly. It shows that, rapid and slow processes are occurring simultaneously. The specific reaction rates for the two processes are obtained by resolving the curve¹² (Table 1A).

Similar experiments were carried out with various iodide ion concentrations ranging from 0.005M to 0.10M. The measurements of lowest iodide concentration were also carried at various temperatures ranging from 25°C to 40°C.

Effect of amount of resin: The experiments as earlier were carried but with different amounts of the resin in the range of 1-5g in 0.005 M iodide ion solution at 25.0°C.

RESULTS AND DISCUSSION

The specific reaction rates at 25.0°C for the two simultaneous processes are 0.156 min⁻¹ and 0.0014 min⁻¹ respectively. It is evident from ion exchange kinetics¹³⁻¹⁴, presumably the first process is film diffusion controlled while the second is particle diffusion controlled. The energy of activation for the film diffusion controlled process is evaluated to be 14.7 KJ mole⁻¹. It is observed that specific reaction rate remains constant even by changing the iodide ion concentration from 0.005M to 0.10M (Table 2). At higher concentration of iodide ion, a lower fraction of radioactive iodide is found to exchange with the resin. From concentration of the iodide ions, the fraction of it exchanged, the specific reaction rate and the initial rate of the exchange is calculated and it is found that this rate varies linearly with the square root of iodide ion concentration.

In second part of study it is observed that the specific reaction rate increases with the amount of the resin. The initial rate of exchange is also evaluated and when this rate is plotted versus the square root of the amount of resin, one does not obtain a straight line; later the rate is found to vary linearly with the amount of the resin. The reason for this is not clear.

The exchange reaction under study can be looked upon as isotopic exchange¹⁵. Hence the amount of the radioactive iodide ions which, has exchanged with the iodide ions in the resin at time 't' is expressed as percentage of the amount initially present in the solution (Table 1.B). From the results, log (1 - F) is plotted versus 't' and here again a composite curve is obtained. This is resolved, as before, into two curves and slope of the first curve is substituted in the equation.

$$\text{Rate of isotope exchange} = 2.303 \frac{a_s a_R}{a_s + a_R} \text{slope}$$

Here 'a_s' and 'a_R' are initial concentrations of the iodide ion in the solution and in the resin respectively. Having thus evaluated rate of isotope exchange (Table 2 and 3), separate curves are plotted for log of rate of isotope exchange versus logarithm of initial concentration of iodide ion in solution and logarithm of rate of isotope exchange versus logarithm of initial concentration of iodide ion in resin. From the isotopes of these curves the orders of isotope exchange versus logarithm of initial concentration of iodide ion in resin. From the slope of these curves the orders of isotope exchange reactions with respect to 'a_s' and 'a_R' are determined. These orders are found to be half each. It is interesting to note that the order of the radioactive isotope exchange is agrees with the order of ion exchange.

Table 1 : Kinetics of ion exchange and isotope exchange of the reaction $RI + I^{*-} \rightleftharpoons RI^{*} + I^{-}$ in Thermax A-127

Concentration of iodide ion in the solution : $5 \times 10^{-3} M$
 Amount of the ion exchange resin : 1.0g.
 Temperature : $25.0^{\circ}C$

(A) Kinetics of the ion exchange.

Time/min	Activity of Solution/CPM	Activity after resolution/CPM	Log(Activity) After resolution	Activity due to slow reaction / CPM	Log (Activity) due to slow reaction
00	13900	7864	3.895	6126	3.787
02	11024	5024	3.701	6090	3.785
04	9712	3725	3.571	6077	3.784
06	8962	3012	3.479	6040	3.781
08	8337	2417	3.383	6010	3.779
10	7741	1861	3.270	5970	3.776
15	6754	804	2.905	5940	3.774
20	4637	333	2.522	5930	3.773
∞	4637	---	----	---	---

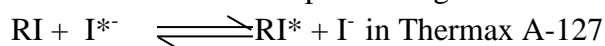
Slope of log (activity after resolution) versus time : $- 67.9 \times 10^{-3} \text{ min}^{-1}$
 Specific reaction rate : 0.156 min^{-1}
 Slope of log (activity due to slow reaction) versus time : $- 1.375 \times 10^{-3} \text{ min}^{-1}$
 Specific reaction rate : 0.0014 min^{-1}

(B) Kinetics of the ion exchange.

Time/m in	% isotope exchange	Fraction Exchanged	(1 - F)	(1 - F) after resolution	Log (1 - F) After solution
2	21.5	0.312	0.688	0.559	- 0.253
4	29.2	0.423	0.577	0.445	- 0.352
6	36.4	0.527	0.473	0.347	- 0.460
8	42.2	0.611	0.389	0.263	- 0.580
10	47.5	0.688	0.312	0.191	- 0.719
15	52.7	0.764	0.234	0.094	- 1.027
20	56.9	0.825	0.175	0.046	- 1.337
00	69.0	1.00	00	-----	-----

Slope of log (1 - F) after resolution versus time : $- 0.058 \text{ min}^{-1}$
 Rate of Exchange : 0.090 min^{-1}

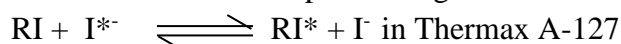
Table 2: Effect of iodide ion concentration on the kinetics of ion exchange and on the rate of isotope exchange reaction



Amount of the ion exchange resin : 1.0 g.
 Volume of the iodide in solution : 200 cm³
 Temperature : 25.0°C

Concentration of iodide ion in solution /M	Milimoles of iodide ion in 200 cm ³ solution	Initial activity in solution/ cpm	Final activity In solution/ cpm	Activity exchanged /cpm	Amount of iodide exchanged/ millimoles	Specific reaction rate/ min ⁻¹	Initial rate of ion exchanged millimole/ min ⁻¹	Rate of isotope exchanged millimole/ min ⁻¹
0.005	1.0	13900	6100	7800	0.561	0.156	0.101	0.090
0.010	2.0	13710	8057	5653	0.825	0.155	0.133	0.133
0.020	4.0	13925	10348	3577	1.03	0.159	0.164	0.175
0.050	10.0	13615	11374	2241	1.65	0.158	0.200	0.241
0.0100	20.0	13515	12507	1008	1.49	0.150	4.211	0.262

Table 3: Effect of the amount of the resin on the Kinetics of ion exchange and on the rate of isotope exchange reaction



Concentration of iodide in the solution : 5 x 10⁻³M
 Amount of iodide ion in 200 cm³ of solution : 1 x 10⁻³ mole
 Temperature : 25.0°C

Amount of Resin/g	Initial activity in solution /cpm	Final activity in solution/cpm	Activity exchanged /cpm	Amount of iodide ion exchanged/ millimole	Specific reaction rate/ min ⁻¹	Initial rate of exchange/ millimole min ⁻¹	Rate of isotope exchange/ millimole min ⁻¹
1	13900	6100	7800	0.561	0.156	0.101	0.090
2	13880	3722	10158	0.731	0.225	0.174	0.141
3	13940	2721	11219	0.807	0.273	0.227	0.195
4	13900	1901	11999	0.863	0.340	0.299	0.172
5	13906	1313	12093	0.870	0.398	0.352	0.237

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