Radioactive Iodine Exchange and the Dushman Reaction

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Critical studies were made on the Dushman reaction, $6H^+ + 5I^- + IO_3^- = 3I_2 + 3H_2O$. Rate measurements of radioactive iodine exchange away from chemical equilibrium gave results which made the rate law for the Dushman reaction doubtful. Measurements of $d(H^+)/dt$ confirmed the rate law. The contrary interpretation resulted because existing chemical information was not considered. This situation holds in many radioactive iodine exchange experiments done on the Dushman reaction.

The reaction between iodate and iodide ions in acid solution was first studied systematically by Dushman.[1)] Its rate law in simplified form was found to be[2,3)]

$$-\frac{[IO_3^-]}{dt} = [IO_3^-][H^+]^2\{2.4\times10^4[I^-]+7.6\times10^{10}[I^-]^2$$
$$+5.5\times10^{10}[I^-][I_3^-]\} \quad \text{at } 25°\text{C} \qquad (1)^{4)}$$

The $[I^-]$ and $[I^-]^2$ terms contribute equally to the rate when $[I^-]$ is near 10^{-7}. The $[I_3^-]$ term is negligible when $[I^-]$ greatly exceeds $[I_3^-]$, which is the case when IO_3^- and I^- are the only iodine species initially mixed.

Measurements of the rate of radioactive iodine isotope exchange have placed Eq. (1) in doubt. Measurements at chemical equilibrium[5-7)] led to different formulations of the $[I^-]$ term. Measurements away from equilibrium in nearly neutral solution by Myers and Kennedy[6)] showed no exchange under conditions where it was expected that the rate of exchange *via* the $[I^-]^2$ term could easily be measured.

A survey of literature on the relevant exchange measurements away from chemical equilibrium[6,8-15)] shows a marked discrepancy (Table 1).

The Dushman reaction participates in the oscillatory decomposition[16)] of H_2O_2. In particular, $[I^-]$ during the $[I^-]$ pulses changes about 10-fold at concentrations where the $[I^-]^2$ term of Eq. (1) contributes significantly to the rate, indicating that the contribution changes by almost 100-fold during a single pulse (see Ref. 16, Fig. 1). Such fluctuations could trigger oscillations. There is no hope of understanding the oscillatory

TABLE 1. RADIOACTIVE EXCHANGE OF IODINE SPECIES WITH IODATE ION

No	Ref.	Species	Acidity	T (°C)	Time	Exchange reported
1	8	I_2	1M	Room (?)	Not given	No
2	8	I_2	20M	"Hot"	Not given	Yes
3	9	I^-	Neutral[a)]	100	3 hr	No
4	10	I_2	Neutral[a)]	Not given	Not given	No
5	10	I^-	Alkaline	Not given	Not given	No
6	6	I^-	Neutral[a)]	50	1600 hr	No
7	11, 12	I_2	Acid	b)	b)	Yes
8[c)]	13	I_2, I^-	pH=5.1	Room (?)	24 hr	Yes
9[c)]	13	I_2, I^-	pH=1	Room (?)	24 hr	No
10	13	I^-	Ammoniac	Room	12 hr	Trace
11	14	I^-	Neutral[a)]	200—300	——	Slow
12	15	I^-	Neutral[a)]	240	up to 24 hr	Yes[d)]

a) Not strictly defined.
b) Equivalent quantities of I^- and IO_3^- in 0.5 M HNO_3 were boiled for 35 min after standing for 40 hr at room temperature.
c) 0.2 mCi ^{131}I added as iodide.
d) Induction period observed.

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4) Concentrations in mol/l actually existing, or calculated to exist, are denoted by ( ). Terms for mol/l added to make the reaction mixture are denoted by [ ]. Time in min.

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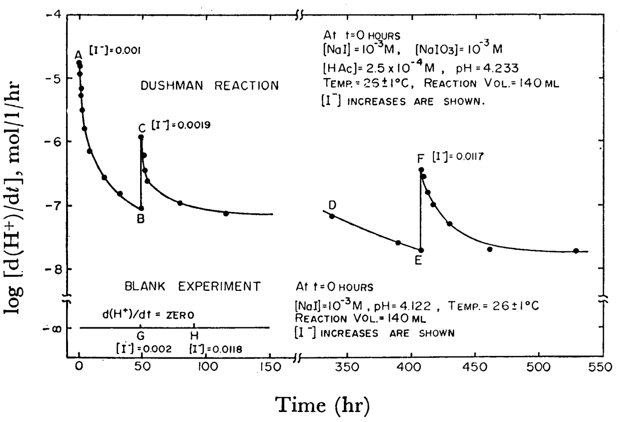

Fig. 1. Decrease of d(H^+)/dt with time in the reaction mixtures of the figure.
Note the breaks in the coordinate axes.

decomposition so long as the present confusion about the Dushman reaction continues.

Experimental

Abel and Stadler[3] carried out their work on the $[I^-]^2$ term in acid solution. Myers and Kennedy[6] used a reaction mixture which they considered nearly neutral. The difference in $[H^+]$ seemed to be responsible for any conflict between the two investigations.

The Dushman reaction may be written as

$$6H^+ + 5I^- + IO_3^- = 3I_2 + 3H_2O \tag{2}$$

Hydrogen ion is rapidly consumed as the reaction proceeds. If the $[H^+]^2$ term in Eq. (1) is correct, the rate of reaction will decrease rapidly as $[H^+]$ decreases. Working near $(H^+)=10^{-7}$ will be difficult because formation of even a small amount of I_2 (or I_3^-) will cause large relative change in (H^+) and thus in the rate. Hence it is desirable to follow the rate by measuring d(H^+)/dt.

Preliminary experiments with $HClO_4$ confirmed the above. Good measurements of d(H^+)/dt could not be made because the rate decreased too rapidly. Measurements in buffered solutions were also difficult. Consequently, acetic acid (HAc) was chosen as a medium between strong acid and buffered solution as regards d(H^+)/dt. It can give rates in reaction mixtures with $[I^-]$ and $[IO_3^-]$ large enough to be considered constant during the experiment.

The reaction mixtures were prepared by mixing NaI, $NaIO_3$, and HAc (J. T. Baker Chemical Co.) solutions. The initial composition is given in Fig. 1. The reaction mixture was contained in a stoppered flask kept in the dark at room temperature except during the pH measurements, which were carried out with a glass electrode (Orion Type 801 Digital Ionalyser). The solution became yellowish as the reaction proceeded. Values of d(H^+)/dt for the logarithmic ordinate of Fig. 1 were obtained by graphical differentiation of the curves of pH against time. Addition of NaI is indicated by points B and E.

A blank experiment was carried out because the oxygen from air can sometimes oxidize I^- to form I_2 and I_3^- with the consumption of H^+. The result was satisfactory.

Discussion of the Results of New Rate Measurements

Figure 1 is qualitatively in accord with Eq. (1): the decreases in rate beyond points A, C, and F point to an $(H^+)^2$ term in the rate law. The perpendicular increases along BC and EF seem in accord with an $(I^-)^2$ term. For a quantitative comparison, one must remember that the progress of reaction is measured by d$\sum(H^+)$/dt, and that

$$\sum(H^+) = (H^+) + (HAc) \tag{3}$$

$$[HAc] = (HAc) + (Ac^-) = 2.5\times10^{-4}\ \mathrm{mol/l} \tag{4}$$

and

$$\frac{(H^+)(Ac^-)}{(HAc)} = 1.8\times10^{-5} \quad \text{at } 25°C \tag{5}$$

from which it follows that

$$\frac{d\sum(H^+)}{dt} = \frac{d(H^+)}{dt} + \frac{d(HAc)}{dt}$$

$$= \frac{d(H^+)}{dt}\left[1+\frac{4.5\times10^{-9}}{\{(H^+)+1.8\times10^{-5}\}^2}\right] \tag{7}$$

The d$\sum(H^+)$/dt calculated by means of Eq. (7) from the measured d(H^+)/dt and (H^+) should be equal to the rate calculated from the rate equation found by Abel and Stadler[3] for HAc solutions.

Agreement is satisfactory (Table 2) considering the difficulties and the fact that Abel and Stadler measured the rate in a different way (iodimetric determination of $-d(IO_3^-)/dt$). We thus conclude that Table 1 contains no evidence that the Dushman reaction does not proceed as expected. It seems clear that all chemical information available should be considered in designing and interpreting radioisotope exchange experiments on this reaction and others.

General Discussion of the Dushman Reaction

Chemical Information. The following three equilibria should be considered.

$$6H^+ + 5I^- + IO_3^- \rightleftharpoons 3I_2 + 3H_2O$$
$$K_8 = 1.6\times10^{47} \quad \text{at } 25°C^{6,17)} \tag{8}$$

$$I_2 + H_2O \rightleftharpoons H^+ + HIO + I^-$$
$$K_9 = 5.4\times10^{-13} \quad \text{at } 25°C^{18)} \tag{9}$$

$$I_3^- \rightleftharpoons I_2 + I^-$$
$$K_{10} = 1.4\times10^{-3} \quad \text{at } 25°C^{19)} \tag{10}$$

In (8), the forward rate is fast in acid solution as Eq. (1) indicates, the reverse rate being slow. For (9) and (10), forward and reverse rates are fast.[20] I_2 does not react directly with IO_3^-.

Isotope exchange between I_2 and IO_3^- cannot occur directly. Exchange between I^- and IO_3^- is possible *via* the Dushman reaction. Equilibria (9) and (10) make an accompanying indirect exchange between I_2 and IO_3^- possible.

Radioactive Iodine Exchange at Chemical Equilibrium. There is no confusion of experimental results for radioactive iodine exchange between I_2 and IO_3^- at chemical

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TABLE 2. QUANTITATIVE EVALUATION OF FIG. 1

	t=0	t=10	t=B	t=C	t=D	t=E	t=F
$(H^+)\times10^5$ (mol/l)	5.85	3.11	2.25	2.20	0.706	0.628	0.600
$(Ac^-)\times10^5$ (mol/l)	5.85	9.11	11.0	11.2	17.9	18.4	18.7
$(HAc)\times10^4$ (mol/l)	1.90	1.57	1.38	1.37	0.70	0.64	0.62
$d(H^+)/dt$ (mol/l/min)[a]	1.9×10^{-5}	6.0×10^{-7}	9.0×10^{-8}	1.2×10^{-6}	8.0×10^{-8}	2.0×10^{-8}	3.8×10^{-7}
$d\sum(H^+)/dt$ (mol/l/min)[b]	3.4×10^{-5}	1.7×10^{-6}	3.4×10^{-7}	4.6×10^{-7}	5.4×10^{-7}	1.4×10^{-7}	2.7×10^{-6}
Calculated rate (mol/l/min)[3]	7.0×10^{-5}	1.7×10^{-5}	8.4×10^{-6}	3.3×10^{-6}	3.1×10^{-6}	2.4×10^{-6}	5.7×10^{-5}

a) Measured $d(H^+)/dt$ from Fig. 1.
b) To be compared with calculated rate.

equilibrium.[5–7] The rate of exchange is[6,21]

$$R=\frac{2\{I_2\}\{IO_3^-\}}{2\{I_2\}+\{IO_3^-\}}\times\frac{\ln 2}{T_{1/2}} \tag{11}$$

where $T_{1/2}$ is the half time for the exchange and R the constant rate, since the system is in chemical equilibrium. For Eq. (11) to be valid, either of the two iodine species added should be initially inactive, and exchange should proceed along a single path which in this case is that of the Dushman reaction. The braces in the equation enclose gram-formula weight of the iodine species.

The measured rates of radioisotope exchange agree fairly well with rates calculated from Eq. (1) for the equilibrium concentrations.[7] Only the $[I^-]$ term is significant in this calculation.

Radioactive Iodine Exchange Away from Chemical Equilibrium. The rate of exchange is determined by Eq. (1), in which the $[I^-]^2$ term has been confirmed. Only the most important case will be discussed.

When radioactive I^- is mixed with excess nonradioactive IO_3^- in acid solution at concentrations such that no solid I_2 is formed, the Dushman reaction will proceed at a rate given by Eq. (1). I_2 and I_3^-, both radioactive, will be produced. As the reaction proceeds, (H^+), (IO_3^-), and (I^-) will decrease, as will the rate of reaction (Fig. 1). As (I^-) decreases, the order of reaction with respect to $[I^-]$ will change as Eq. (1) requires. (I_3^-) will decrease along with (I^-) in conformity with Equilibrium (10). Radioactive IO_3^- will begin to form when steps in the reverse Dushman reaction begin to proceed at an appreciable rate. In equilibrium, forward and reverse rates will be equal, and Eq. (11) will hold.

Experiment 127 of Myers and Kennedy. Myers and Kennedy[6] reported that in an extention of their equilibrium exchange measurements to higher iodide concentrations, Experiment 127 was performed with $[NaI]=5\times10^{-3}$ and $[NaIO_3]=0.1$ in nearly neutral solution at 50 °C. No measurable exchange was found in any of the five samples of solution taken over a period of 1600 hr. They concluded that $T_{1/2}$ in Eq. (11) exceeded 5×10^5 hr at 50 °C.

By use of Eq. (11), they calculated the expected $T_{1/2}$ of 2.8×10^4 hr at 25 °C for the experiment. The calculation is not acceptable because their system was not in equilibrium. They used a value of R calculated from the $[I^-]^2$ term of Eq. (1) with $(H^+)=10^{-7}$. As (H^+) is drastically reduced during the approach to chemical equilibrium, the rate at equilibrium should be far less than their value of R to obtain $T_{1/2}=2.8\times10^4$ hr.

It is possible to calculate the expected equilibrium rate for Experiment 127. Here H_2O plays somewhat the same role as HAc in Fig. 1, and OH^- is analogous to Ac^-. Here the Dushman reaction is

$$3H_2O+5I^-+IO_3^-=3I_2+6OH^- \tag{12}$$

Further, Equilibrium (10) requires that 3.6 mol of I_3^- form at 25 °C for each mole of I_2, which means that 2×4.6 mol OH^- will be formed for each mole of I_2 produced in Reaction (12). Thus

$$(OH^-)_{eq}=10^{-7}+9.2\times(I_2)_{eq} \tag{13}$$

for an initially neutral reaction mixture that has gone to equilibrium. Obviously,

$$(H^+)_{eq}=\frac{10^{-14}}{10^{-7}+9.2\times(I_2)_{eq}}\quad\text{at }25^\circ\text{C} \tag{14}$$

For known $[I^-]$ and $[IO_3^-]$, Equilibrium (8) gives the relation of $(H^+)_{eq}$ to $(I_2)_{eq}$ because

$$K_8=\frac{(I_2)^3}{(H^+)^6(I^-)^5(IO_3^-)}=1.6\times10^{47}\quad\text{at }25^\circ\text{C} \tag{15}$$

The last two equations give the rounded values $(I_2)_{eq}=7.6\times10^{-7}$ and $(H^+)_{eq}=1.4\times10^{-9}$ for Experiment 127. The expected value of $T_{1/2}$ is

$$T_{1/2}=2.8\times10^4\left\{\frac{10^{-7}}{1.4\times10^{-9}}\right\}^2=1.4\times10^8\text{ hr}\quad\text{at }25^\circ\text{C} \tag{16}$$

The expected half time $T_{1/2}$ at 50 °C will be lower, perhaps 10-fold lower, than the value in Eq. (16). This lower half time still exceeds 5×10^5 hr. Therefore, our calculated value is in accord with the results of Experiment 127.

There is thus no conflict between the results of Experiment 127 and the $[I^-]^2$ term in Eq. (1). Considerations about mechanism[6,22] that assumed such a conflict are invalid. To verify the $[I^-]^2$ term by measuring the rate of isotope exchange, one ought to make the measurements on reaction mixtures at chemical equilibrium.

In order to clarify the discrepancies in Table 1, each conclusion therein should be examined as in Experiment 127, and all available chemical information be given due consideration.

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