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Rate of the Dushman Reaction in Iodic Acid at Low Iodide Concentration. Complexity of Iodic Acid

Ryusaburo Furuichi* and Herman A. Liebhafsky

Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

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Three rate laws have been postulated for the Dushman reaction, $6H^+ + 5I^- + IO_3^- = 3H_2O + 3I_2$, with total reaction orders of four, five and six, at iodide ion concentrations below 10^{-8} M. New direct measurements of the rate and an examination of thermodynamic data for iodic acid solutions have eliminated some of the confusion. The complexity of iodic acid solutions, with and without added salt, makes it impossible to establish a single reaction order from the radioactive iodine exchange measurements. The new results are best expressed by a quasiempirical rate equation, $-d[IO_3^-]/dt = 8.59 \times 10^4 [H^+]^2 (I^-)[IO_3^-]$ mol l^{-1} min^{-1}, which is closely approximated by $-d[IO_3^-]/dt = \gamma_{\pm p}^4 (H^+)^2 (I^-)(IO_3^-)\{k' + k''(HIO_3)\}$ mol l^{-1} min^{-1}, with $k' = 2.83 \times 10^5$ mol^{-3} l^3 min^{-1} and $k'' = 6.60 \times 10^6$ mol^{-4} l^4 min^{-1} for 25 °C. The second rate law is interpreted in terms of a reasonable mechanism that takes into account the thermodynamically established polymerization in iodic acid solutions.

A series of preliminary investigations[1-4] into the oscillatory decomposition of hydrogen peroxide by iodine species has shown that the decomposition is accompanied by oscillatory changes in iodine concentration and that the Dushman reaction,

$$6H^+ + 5I^- + IO_3^- = 3I_2 + 3H_2O \qquad (1)$$

participates in the oscillations. For Reaction (1), three rate laws[5-7] have been reported in which the total reaction order is four, five and six, respectively. The first rate law is based on direct rate measurements of iodine formation and an assumption that iodic acid is a strong electrolyte. This rate law gave smaller calculated rate values than those obtained in our experiments. The last two rate laws[6,7] are based on the measurements of rates of radioactive iodine exchange ($I^{131}I + IO_3^- = I_2 + {}^{131}IO_3^-$), which is an indirect method since the measurements are carried out at chemical equilibrium of Reaction (1). These rate laws were derived by using the stoichiometric activity coefficient of iodic acid measured by Abel, Redlich and Hersch[8] which shows unusual change of degree of dissociation with change in concentration of the acid (Fig. 2).

On the other hand, the results of direct rate measurements[9] gave a quasiempirical rate law, satisfactory up to 50 °C.

$$-\frac{d[IO_3^-]}{dt} = k_2'[H^+]^2(I^-)[IO_3^-] \qquad (2)$$

in which concentrations in M actually existing, or calculated to exist are donoted by ( ) and terms for M added to make the reaction mixture are denoted by [ ]. Equation (2) gave calculated rates in sharp conflict with those from the two rate laws established by the radioactive iodine exchange study. However, Eq. (2) does not establish the mechanism of Reaction (1).

The present investigation was undertaken in the hope of explaining some of this disquieting confusion about the Dushman reaction and its mechanism. Emphasis is placed on the thermodynamic complexity of iodic acid solutions, the radioactive exchange data has been re-examined, and new direct rate measurements are made under the simplest possible conditions; *i. e.*, for the most part, in reaction mixtures consisting of iodic acid (0.137—0.833 M) in equilibrium with solid silver iodide and solid silver iodate to maintain the iodide ion concentration constant below 10^{-9} M.

Experimental

Measurements were carried out by a method similar to that already described[9] and are summarized here. Thirty grams of solid AgI, 10 ml of 10^{-2} M-$AgNO_3$ solution and 80 ml of deionized water were mixed in the reaction vessel[10] and stirred at a rate of 1600 rpm in a thermostated water bath. Ten milliliter of HIO_3 solution was then added to start the reaction. The reaction time was measured after 5 ml of the acid has been added. All the reagents were of analytical grade (J. T. Baker Chem. Co.).

Ten seconds prior to each sampling, stirring was stopped and

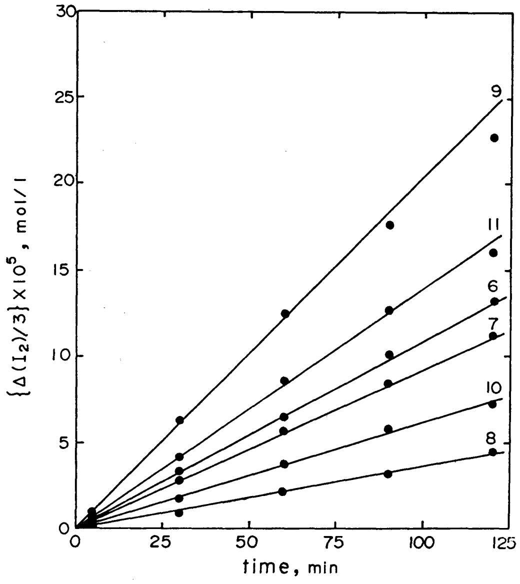

Fig. 1. Rate of the Dushman reaction measured in iodic acid solutions at 25 °C.
Concentrations of iodic acid solutions used are shown in Table 1 for experiments numbered 6—11.
Amount of silver iodide: 30 g/100 ml-solution, Initial silver nitrate concentration: 10^{-3} M, Stirring speed: 1600 rpm.

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* Present address: Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060 Japan.

solid AgI was allowed to settle, which halted the reaction. The solution, 3 ml, was then withdrawn with a syringe and discharged into a small separatory funnel containing 4 ml of CCl_4. The iodine was extracted by shaking for 3 min, and the CCl_4 was transferred to a cuvette and centrifuged for 1.5 min to separate residual solid AgI. The content of I_2 in CCl_4 was spectrophotometrically determined from the absorbance at 500 nm (Hitachi-Perkin-Elmer Double-Beam Type Spectrophotometer).

The iodide ion concentration of the reaction mixture was maintained at constant values below 10^{-9} M by the establishment of the solubility equilibria of AgI[11] and $AgIO_3$[12]. The concentration of H^+ and IO_3^- were also practically constant, since the amount of I_2 formed by the reaction was sufficiently small. The rate of reaction was estimated from the linear relation between the amount of formed I_2 and the time (Fig. 1.). In order to test the salt effect on the rate, five measurements were carried out at 5 °C in solutions containing 1.035 M-$LiClO_4$. In no experiment was formation of solid I_2 observed.

Results and Discussion

Estimation of Rate for 25 °C. The results of the measurements are summarized in Table 1. Rate constant k_2' for Eq. (2) was calculated[13] from the measured rates at 5, 25, 30, and 50 °C.

The reaction order and rate constant should be evaluated from the results of measurements over a sufficiently wide range of iodic acid concentration. However, since the reaction is of high order, an adequate concentration range could not be covered satisfactorily at one temperature. Consequently, the results of measurements carried out at suitably different concentrations over the temperature range 5—50 °C were converted into those at 25 °C for a final test of the different rate laws by the following method.

For each temperature (Table 1), mean values of the k_2' values lie very near the line defined by

$$\log k_2' = \frac{-1.612\times 10^3}{T} + 10.339 \qquad (3)$$

The numerical values compare favorably with 1.628×10^3 and 10.504, which appear in the corresponding equation[9] for reaction mixtures prepared by using sodium iodate and perchloric acid instead of iodic acid. Over the temperature range, the two equations obtained by these two sets of values give almost identical values of k_2' since the numerical differences between the equations tend to compensate. There can be no doubt that the conversion of the newly measured k_2' values into those at 25 °C is reliable. Except at high concentrations, constancy of the $k_2'_{(25°)}$ values is reasonably good. The mean value of the $k_2'_{(25°C)}$ values is 8.59×10^4 mol^{-3} l^3 min^{-1}, to be compared with 11.80×10^4 mol^{-3} l^3 min^{-1}, the corresponding results from the (sodium iodate+perchloric acid) system.[9]

Thermodynamic Complexity of Iodic Acid. Iodic

Table 1. Results of direct rate measurements in iodic acid solution

No.	React. temp.	$[HIO_3]$[a) M	Meas·rate × 10^7 mol l^{-1} min^{-1}	$k_2' \times 10^{-4}$ [b) l^3 mol^{-3} min^{-1}	$k_2'_{(25°C)} \times 10^{-4}$ [c) l^3 mol^{-3} min^{-1}
1	5 °C	0.343	2.30	4.26	10.42
2		0.595	13.60	3.23	7.90
3		0.833	38.10	2.62	6.41
4		0.457	6.50	4.11	10.05
5		0.714	27.00	3.27	8.00
				av. 3.50	av. 8.56
6	25 °C	0.300	11.00	8.48	8.48
7		0.286	9.35	8.70	8.70
8		0.2285	3.75	8.04	8.04
9		0.343	20.50	9.65	9.65
10		0.259	6.25	8.36	8.36
11		0.318	14.00	8.38	8.38
				av. 8.60	av. 8.60
12	30 °C	0.2285	7.20	10.78	8.79
13		0.286	16.00	10.18	8.30
				av. 10.48	av. 8.55
14	50 °C	0.114	3.60	19.51	7.51
15		0.2285	61.00	23.60	9.67
16		0.194	32.50	23.81	9.15
17		0.174	19.80	23.15	8.90
18		0.137	7.80	21.17	8.14
				av. 22.25	av. 8.67
Salt effect measurements					
19	5 °C	0.343	1.98	$[LiClO_4]=1.035$ M	
20		0.475	5.80		
21		0.595	12.34		
22		0.714	20.37		
23		0.833	34.32		

a) Since 10^{-3} M silver nitrate was added to the reaction mixture, iodate ion concentration was less by this amount than hydrogen ion concentration. The difference was taken into account in the calculation. b) Calculated from Eq. (2) and measured rates at each temperature. Values of (I^-) from Ref. 9, Eq. (6) with correct equilibrium constants for each temperature. Constants for 25 °C appear in Table 2, footnote b). c) Calculated from Eq. (3).

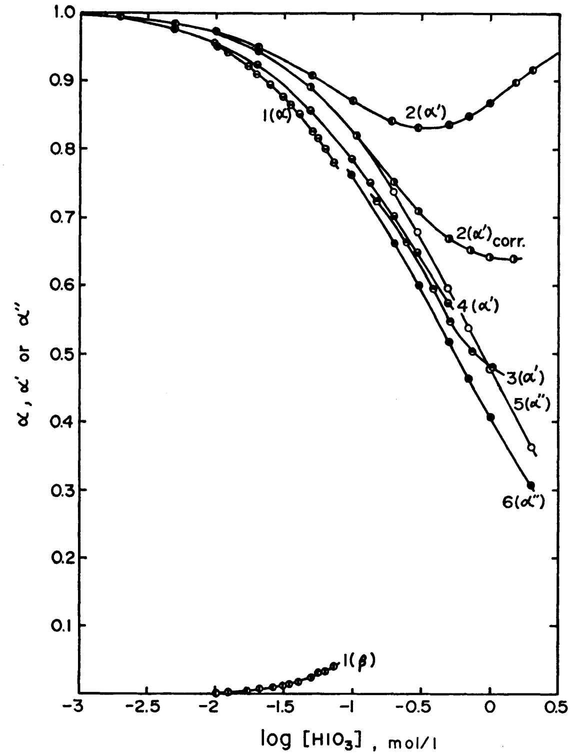

Fig. 2. Degree of dissociation of iodic acid. $1(\alpha)$ and $1(\beta)$: data of Ref. 14, Table 5, 25 °C (⊖, ⦶), $2(\alpha')$: calculated from γ_s data from Ref. 8, 0 °C, (cryoscopic data) (◐), $2(\alpha')_{\text{corr}}$: $2(\alpha')$ corrected for $HI_2O_6^-$ formation (◑), $3(\alpha')$: calculated from data of Ref. 16, 33 °C, (Raman-spectrum data) (◓), $4(\alpha')$: calculated from data of Ref. 8, 18 °C, (conductivity data) (◒), $5(\alpha'')$: calculated with $K=0.258$[9] in Eq. (11), 0 °C (○), $6(\alpha'')$: calculated with $K=0.165$[9] in Eq. (11), 25 °C (●).

acid is an intermediate electrolyte, neither weak nor strong, and the complexity of its aqueous solutions is further increased by the formation of various polymers of pentavalent iodine, *e.g.*, the dimers $H_2I_2O_6$ and $HI_2O_6^-$. The complexity is of thermodynamic and kinetic importance. Results of thermodynamic examination are given in Fig. 2.

Pethybridge and Prue[14] gave a precise thermodynamic treatment of the dissociation equilibrium of iodic acid ($HIO_3 \rightleftharpoons H^+ + IO_3^-$) and the formation of polymer ($HIO_3 + IO_3^- \rightleftharpoons HI_2O_6^-$), below 0.1 M at 25 °C on the basis of the Debye-Hückel equation and of Eqs. (4)—(6),

$$K = \frac{(\gamma_\pm)^2(H^+)(IO_3^-)}{(HIO_3)} = \frac{\alpha(\alpha-\beta)(\gamma_\pm)^2[HIO_3]}{(1-\alpha-\beta)} = 0.157\ \text{mol l}^{-1} \tag{4}$$

$$K_1 = \frac{(HI_2O_6^-)}{(HIO_3)(IO_3^-)} \tag{5}$$

$$= \frac{\beta}{(\alpha-\beta)(1-\alpha-\beta)[HIO_3]} = 4.1\ \text{mol}^{-1} \tag{6}$$

where K is the acidity constant, K_1 the stability constant of $HI_2O_6^-$, $[HIO_3]$ the formal concentration of iodic acid added to make the solution, α is the degree of dissociation $((H^+)/[HIO_3])$, β $(HI_2O_6^-)/[HIO_3]$, and $\gamma_\pm$ the activity coefficient. The values of α and β measured by Pethybridge and Prue are shown in Fig. 2, Curves $1(\alpha)$ and $1(\beta)$.[14]

Three other results for iodic acid solution are expressed by defining the degree of dissociation α' by

$$K = \frac{(\gamma_s)^2[HIO_3]}{(1-\alpha')}, \text{ Cryoscopy}^{8)} \tag{7}$$

where γ_s is the stoichiometric activity coefficient and equal to $\gamma_\pm\alpha'$,

$$\gamma_s = \gamma_\pm\alpha' \tag{8}$$

$$K_c = \frac{(H^+)(IO_3^-)}{(HIO_3)} = \frac{(\alpha')^2[HIO_3]}{(1-\alpha')}, \text{ Conductivity}^{8)} \tag{9}$$

$$(IO_3^-) = \alpha'[HIO_3], \text{ Raman-spectrum}^{16)} \tag{10}$$

The calculated values of α' on the basis of data in Refs. 8 and 16, and of Eqs. (7)—(10) are shown in Fig. 2, Curves $2(\alpha')$, $3(\alpha')$ and $4(\alpha')$.

The minimum of Curve $2(\alpha')$ (Fig. 2) and the high values of α' would be due to polymerization in iodic acid solutions. In the treatment of Pethybridge and Prue,[14] only the dimer $HI_2O_6^-$ was considered giving

$$(\gamma_s)^2 = (\gamma_\pm)^2\alpha(\alpha-\beta). \tag{8a}$$

This equation was used to correct Curve $2(\alpha')$; β is the vertical distance between this curve and Curve $2(\alpha')_{\text{corr}}$. Figure 2 shows that the correction is not adequate.

The thermodynamic data for iodic acid solutions above 0.1 M are still uncertain and the solutions are highly complex. Curves $5(\alpha'')$ and $6(\alpha'')$ in Fig. 2 show a degree of dissociation for 0 and 25 °C which was calculated by trial-and-error method by the equation,

$$K = \frac{(\gamma_{\pm p})^2(\alpha'')^2[HIO_3]}{(1-\alpha'')} \tag{11}$$

where $\gamma_{\pm p}$ is the mean activity coefficient of perchloric acid[15] and K the dissociation constant of iodic acid from Ref. 9, Eq. (17). This newly defined α'' is quasi-empirical, but it seems to give reasonable values and a reasonable change with the concentration up to 1 M. Accordingly, for calculating (H^+), (IO_3^-) and (HIO_3), Curves $1(\alpha)$ and $6(\alpha'')$ are used in concentration ranges below and above 0.1 M, respectively. The values of concentrations thus calculated are given in Table 2.

Comparison of Rate Laws. New rate measurements were carried out in order to obtain results that could remove confusion concerning the rate law of the Dushman reaction at iodide ion concentrations below 10^{-8} M. The thermodynamic complexity of iodic acid solutions (Fig. 2) and the lack of thermodynamic data for such solutions containing added salt make the assignment complicated. A comparison of rates calculated for 25 °C from various rate laws is given in Table 3, at each iodic acid concentrations shown in Table 2. In the calculation of rates, it is assumed that $\gamma_{\pm(HIO_3)} = \gamma_{\pm(HI)} = \gamma_{\pm p}$ for a comparison of the different rate laws.

New rates, calculated according to Eq. (2) by use of the $k_2'{}_{(25\,^\circ C)}$ values (Table 1) are given in Table 3. They were calculated from

TABLE 2. CALCULATED CONCENTRATIONS FOR 25 °C

No.	(H^+)[a] M	(IO_3^-)[a] M	(HIO_3)[a] M	$(I^-)\times 10^{10}$ [b] M	$\gamma_{\pm p}$
1	0.198	0.197	0.145	5.29	0.778
2	0.292	0.291	0.303	7.80	0.769
3	0.362	0.361	0.471	9.66	0.766
4	0.244	0.243	0.213	6.52	0.773
5	0.329	0.328	0.385	8.80	0.767
6	0.180	0.179	0.120	4.80	0.781
7	0.173	0.172	0.113	4.62	0.782
8	0.147	0.146	0.0815	3.93	0.787
9	0.198	0.197	0.145	5.29	0.778
10	0.162	0.161	0.097	4.33	0.784
11	0.195	0.194	0.123	5.20	0.779
12	0.147	0.146	0.0815	3.93	0.787
13	0.173	0.172	0.113	4.62	0.782
14	0.0854	0.0844	0.0289	2.26	0.810
15	0.147	0.146	0.0815	3.93	0.787
16	0.1305	0.1295	0.0638	3.48	0.792
17	0.1184	0.1174	0.0530	3.15	0.795
18	0.0989	0.0979	0.0383	2.63	0.803

a) Calculated by trial-and-error from Eq. (11) with $K=0.165$[9] and $\gamma_{\pm p}$[15] at 25 °C (Column 6). b) Calculated from Eq. (6) in Ref. 9 with $K=0.165$; with 8.591×10^{-17} as the solubility product of silver iodide[11]; and with 3.199×10^{-8} as the solubility product of silver iodate.[12]

TABLE 3. COMPARISON OF RATES CALCULATED FOR 25 °C FROM VARIOUS RATE LAWS

No.	Rate $\times 10^7$ mol l^{-1} min^{-1}				
	Eq. (2)[a]	Eq. (12)	Eq. (13)	Eq. (14)	Eq. (19)
1	22.17	23.80	120.9	4.49	18.57
2	129.54	183.0	1163	62.15	154.57
3	357.27	625.0	4126	177.0	533.93
4	62.39	69.30	408.1	25.31	56.90
5	255.72	357.3	2348	113.0	299.19
6	11.00	14.45	69.61	5.51	11.16
7	9.35	12.04	55.35	4.53	9.11
8	3.75	4.99	21.61	2.01	3.93
9	20.50	23.80	120.9	4.49	18.57
10	6.25	8.37	38.48	3.26	6.38
11	14.00	18.63	110.9	8.24	15.49
12	4.13	4.99	21.61	2.01	3.93
13	9.20	12.04	55.35	4.53	9.15
14	0.25	0.38	0.94	0.13	0.28
15	4.23	4.99	21.61	2.01	3.93
16	2.31	2.50	10.07	1.10	2.13
17	1.40	1.76	6.22	0.68	1.31
18	0.55	0.75	2.34	0.27	0.56

a) Calculated from $k'_{2(25^\circ\mathrm{C})}$ in given Table 1, by use of Eq. (2). For iodic acid solutions, the right-hand side of Eq. (2) equals to $k_2'[HIO_3]^3(I^-)$. This simple form is not quite applicable here. See Table 1, footnote a).

$$-\frac{d[IO_3^-]}{dt} = 11.18\times10^4[IO_3^-](I^-)[H^+]^2 \ \mathrm{mol\ l^{-1}\ min^{-1}} \tag{12}$$

which represents the results of our direct rate measurements[9] on reaction mixtures made from perchloric acid and sodium iodate. The agreement between the two sets of rate is good except at higher concentrations of the acid where thermodynamic complexities are to be expected.

Rates for Eqs. (13) and (14) are based on the results of measurements of the rate of exchange of radioactive iodine at chemical equilibrium (an indirect method); those for Eq. (13) were calculated from

$$-\frac{d(IO_3^-)}{dt} = (\gamma_{\pm p})^6(IO_3^-)(I^-)(H^+)^3\{4.42\times10^8(IO_3^-) + 6.60\times10^6(ClO_4^-)\} \ \mathrm{mol\ l^{-1}\ min^{-1}} \tag{13}$$

which is given by Myers and Kennedy[7] and those for Eq. (14) were calculated from

$$-\frac{d(IO_3^-)}{dt} = 1.1\times10^6(IO_3^-)(I^-)(H^+)^3 \ \mathrm{mol\ l^{-1}\ min^{-1}} \tag{14}$$

which is given by Connick and Hugus.[6]

The rates calculated by Eq. (14) are only a small fraction of those by Eq. (13), which means that the two investigations using radioactive iodine do not agree with each other. The rates obtained from the direct rate measurements all fall between the corresponding data based on the radioactive exchange measurements. In part, the divergences result from different ways of dealing with salt effects. Connick and Hugus[6] assumed that these effects would not vary at constant, high ionic strength; the assumption has not been confirmed. Myers and Kennedy[7] followed Randall and Allen[17] in defining the activity coefficient of iodic acid, and used $\gamma_\pm$ obtained from freezing-point data.[8] The procedure ignores polymerization and relies on the unreasonable α' values of Curve 2(α'). The rate of radioactive iodine exchange in the present system is given by

$$\begin{aligned} R &= k_a(I_2)^{0.6}(IO_3^-)^n(H^+)^p(\gamma_\pm)^{n+p} \\ &= k_a(I_2)^{0.6}[HIO_3]^{n+p}(\alpha)^{n+p}(\gamma_\pm)^{n+p} \end{aligned} \tag{15}$$

where R is the exchange rate, n and p are the reaction orders. The other symbols were defined previously. This is the starting point for Eq. (13), and the rate

$$\begin{aligned} R &= k_c(I_2)^{0.6}(IO_3^-)^n(H^+)^p \\ &= k_c(I_2)^{0.6}[HIO_3]^{n+p}(\alpha)^{n+p} \end{aligned} \tag{16}$$

may serve similarly as a starting point for Eq. (14). Since the Dushman reaction (Eq. (1)), with the following equilibrium constant at 25 °C[18]

$$\frac{(I_2)^3}{(\gamma_\pm)^{12}(H^+)^6(I^-)^5(IO_3^-)} = 10^{47.2} \tag{17}$$

was assumed to be in equilibrium during course of the radioactive exchange reaction, the term $(I_2)^{0.6}$ can be eliminated from Eqs. (15) and (16), as follows;

$$\begin{aligned} (I_2)^{0.6} &= 10^{47.2/5}(\gamma_\pm)^{12/5}(IO_3^-)^{1/5}(H^+)^{6/5}(I^-) \\ &= 10^{9.44}(\gamma_\pm)^{2.4}(\alpha)^{1.4}[HIO_3]^{1.4}(I^-) \end{aligned} \tag{18}$$

Under the simplest conditions, the total order of a reaction is independent of concentration and temperature. Calculations were carried out to see whether this would hold in the present case when the total order was established according to Myers and Kennedy.[7] Figure 3 shows the logarithm of the exchange rate R as a function of $\log \gamma_{\pm p}\alpha''[HIO_3]$ at 0, 25, and 50 °C, the α'' being calculated from Eq. (11) for each temperature.[9] From Eqs. (15) and (18), the total reaction order is given by $(n+p+2.4)$; thus the slopes of the lines in Fig. 3 indicate a change

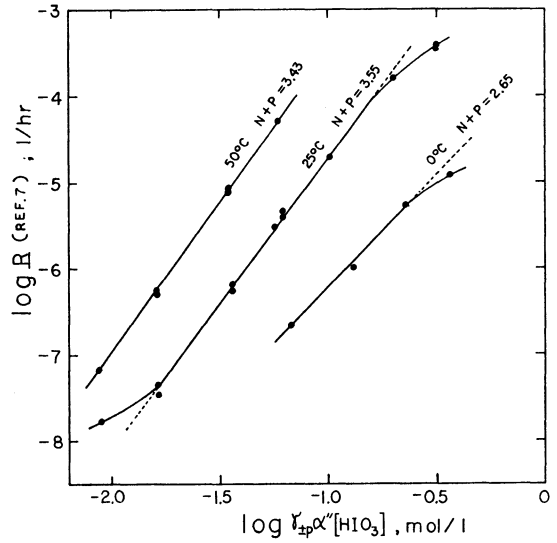

Fig. 3. Re-evaluation of radioactive iodine exchange rate data from Ref. 7.

in total order from 5.05 to 5.95. A similar plot for the rates obtained in direct rate measurements gave a similar result: the total order[19] varied systematically; *i.e.*, 4.7 at 5 °C, 5.04 at 25 °C, 5.14 at 30 °C, and 5.22 at 50 °C.

The most precise way of determining the total order from R values is to use the thermodynamic data of Pethybridge and Prue,[14] which are definitive in the concentration range below $[HIO_3]=0.1$ M, and of R values measured by Myers and Kennedy[7] for solutions of 0.05 and 0.1 M. The thirteen applicable R values were corrected to these iodic acid concentrations and to $(I_2)=10^{-3}$ M. It was found that, at $[HIO_3]=0.1$ M, the mean R value of 4.167×10^{-6} hr^{-1} was obtained for nine data ranging from 3.970×10^{-6} to 4.297×10^{-6} hr^{-1}; at $[HIO_3]=0.05$ M, the mean R value of 0.5916×10^{-6} hr^{-1} was obtained for four data ranging from 0.5510×10^{-6} to 0.6542×10^{-6} hr^{-1}. These means are close to the values of 3.93×10^{-6} and 0.616×10^{-6} hr^{-1}, which were calculated by the equation for R at 25 °C,[7] $R=7.40(\gamma_{\pm p})^{3.6}(I_2)^{0.6}(IO_3^-)^{1.8}(H^+)^{1.8}$ hr^{-1}, in which $n=p=1.8$ was used. Re-evaluation of total order can be made by using these mean R values and Eqs. (15) and (16) with $(\alpha-\beta)^n$ replacing $(\alpha)^n$ to allow for the formation of $HI_2O_6^-$, which was assumed to be inert toward iodide ion. The total order may then be obtained from the ratio between mean R values at $[HIO_3]=0.1$ and 0.05 M, provided that an order with respect to iodate ion concentration is assumed. The results of the calculations are summarized in Table 4, which show total reaction orders not far from six in iodic acid solutions below 0.1 M.

Table 4. Total reaction order $(n+p+2.4)$ of radioactive exchange rate estimated from data[14] at $[HIO_3]=0.05$ and 0.1 M.

Assumption[7]	$n=0.8$	$n=p$
Concentration calculation (Eq. (16))	5.87[a]	5.94
Activity Calculation (Eq. (15))	6.24	6.36[b]

a) Corresponding value from Ref. 6 is 5; *i.e.* $(H^+)^3(IO_3^-)(I^-)$. b) Corresponding value from Ref. 7 is 6; *i.e.* $(H^+)^3(IO_3^-)^2(I^-)$.

The radiochemical-exchange results do not give a single, constant total order applicable to the Dushman reaction over a wide range of conditions. The complexity of iodic acid solutions is mainly responsible.

Effect of Added Perchlorate. In order to test the dependence of perchlorate ion concentration required by Eq. (13), five experiments at 5 °C were repeated with reaction mixtures containing 1.035 M of lithium perchlorate (Table 1, Nos. 19—23). The addition of this salt always gave reduced rates: the ratios of rates in the solution containing lithium perchlorate to the corresponding rates obtained from Nos. 1—5 were found to be 0.86, 0.89, 0.91, 0.77, and 0.90, respectively. Furthermore, in the radioactive exchange experiments given in Ref. 7, Table 3, R values of 20.2, 20.4, 20.1, and 14.8×10^{-6} hr^{-1} were obtained for $[HIO_3]=0.2$ M at $[NaClO_4]$ values of 0, 0, 0.053, and 2.000 M, respectively. Both sets of results indicate a 10—25% reduction in rates; this proves that Eq. (13) does not hold. The measured salt effect in this system is small for an ionic reaction of high order.

New Rate Law and Reaction Mechanism. No single, satisfactory reaction order can be found for the Dushman reaction at iodide ion concentration below 10^{-8} M. The quasiempirical rate law, Eq. (2), is the most satisfactory from the results given in Tables 1—3.

The existence of polymeric pentavalent iodine species is indicated by Fig. 2. The work of Pethybridge and Prue[14] supports the existence of a dimeric species, $HI_2O_6^-$, in dilute iodic acid solutions. It is natural to assume that all such species can react with iodide ion. Such reactions would increase the order of the reaction with respect to iodic acid or iodate ion. If only a dimeric species is assumed to react, the expected rate law would have the form

$$-\frac{d[IO_3^-]}{dt}=(\gamma_{\pm p})^4(H^+)^2(IO_3^-)(I^-)\{k'+k''(HIO_3)\} \quad (19)$$

In order to test this equation, the 25 °C rates given for Eq. (2) in Table 3 were divided by $(\gamma_{\pm p})^4(H^+)^2(IO_3^-)(I^-)$, calculated by use of the values in Table 2, and plotted as a function of (HIO_3) at 25 °C. The results (Fig. 4) show a line that gives $k'=2.83\times10^5$ mol^{-3} l^3 min^{-1} and $k''=6.60\times10^6$ mol^{-4} l^4 min^{-1}. The data scatter to some extent at (HIO_3) values above 0.12 M. The rates calculated by use of Eq. (19) with the numerical values of k' and k'' are listed in Table 3. They agree fairly well with those obtained from Eq. (2).

We believe that Eq. (19) gives an improvement on the rate law for the Dushman reaction at low iodide ion concentrations, and that it can replace the other rate laws to establish the reaction mechanism. It should be noted that (HIO_3) can always be replaced by $K(\gamma_\pm)^2(H^+)(IO_3^-)$ because the dissociation of iodic acid is rapid and reversible. It is thus not possible to confirm whether only iodic acid molecule, or only its ions, react; or whether both reaction paths exist. For the sake of simplicity, iodic acid molecule is assumed to be the reacting species, a similar assumption being made for $H_2I_2O_6$. The following

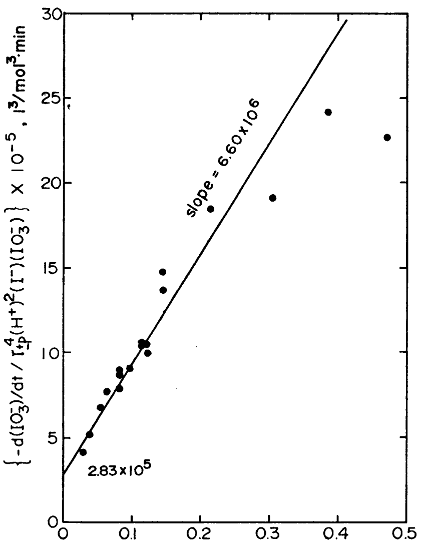

Fig. 4. Plots of Eq. (19) and estimation of the rate constants for 25 °C.
The values of rate, $\gamma_{\pm p}$ and concentrations necessary for the calculations are shown in Table 2, and Table 3, Column 2.

parallel kinetic paths are then postulated to explain Eq. (19);

Monomeric-pentavalent-iodine path (k'; intercept in Fig. 4):

Rapid reversible reaction:

$$H^+ + I^- + HIO_3 \rightleftharpoons H_2I_2O_3 \qquad (20)$$

Rate-determining step:

$$H_2I_2O_3 \longrightarrow HIO + HIO_2 \qquad (21)$$

Dimeric-pentavalent-iodine path (k''; slope in Fig. 4)
Dimerization equilibrium:

$$2HIO_3 \rightleftharpoons H_2I_2O_6 \rightleftharpoons H^+ + HI_2O_6^- \qquad (22)$$

Rate-determining step:

$$H^+ + I^- + H_2I_2O_6 \longrightarrow 3HIO_2 \qquad (23)$$

The mechanism should includes the dissociation equilibria of iodic acid. It is completed by the rapid reactions of hydrogen ion and iodide ion with hypoiodous acid and iodous acid to form iodine. The reactive intermediate species $H_2I_2O_3$ has been proved to be useful.[3,10,20–24] The work of Pethybridge and Prue[14] makes $H_2I_2O_6$ (or $HI_2O_6^-$) more logical for the dimeric-pentavalent-iodine path than $IO_2^+IO_3^-$ (closely related to I_2O_5), postulated by Myers and Kennedy.[7] Our mechanism for this path is simpler than that of Edwards,[25] in which iodate ion is assumed to react with I_2O_2 (dehydrated $H_2I_2O_3$) in the rate-determining step.

The present investigation has shown that the confusion concerning the Dushman reaction mainly arises from the complexity of iodic acid solutions, which leads to proposed rate laws that can not be verified by direct measurements of the rate. However, the usefulness of radioactive-exchange measurements in simpler systems is recognized.

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