of the similarity in the spectra of the two substances. In this connection it is interesting that the sum of the moles of carbon monoxide and of ketene is less than one only in the case of run 27. The values given in Table III for this run give good agreement, however, which may be taken as an indication that the amount of methyl ethyl ketone formed in this run is small.

Acknowledgments.—The authors wish to express appreciation for a grant received from the Research Corporation of New York. They are also indebted to the Research Committee of the University of Utah for funds used to purchase the Burrell gas analysis apparatus.

Summary

The present investigation points out a number of facts that should prove of importance in the study of this and other photochemical reactions.

1. Ketene is formed in the photolysis of acetone in a flow system under the proper conditions and at temperatures much lower than those required for its preparation by pyrolysis. This is of importance in view of the assumption at the time of the publication of Noyes and Dorfman[3] that all of the products were known.
2. Ultraviolet spectra have been found useful in identifying and measuring ketene trapped with unreacted acetone.
3. Competing over-all reactions are proposed to fit the relative quantities of products obtained in the high temperature photolysis of acetone.
4. A flow system for photochemical studies has the same relative advantages as for pyrolytic work, enabling the detection of primary products.

SALT LAKE CITY, UTAH RECEIVED AUGUST 5, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Kinetics of the Iodine–Iodate Isotopic Exchange Reaction

BY ORLO E. MYERS[1] AND JOSEPH W. KENNEDY

The exchange of iodine atoms between aqueous iodine and iodate ion has been reported as being a slow reaction.[2] Radioactive I^{131} has been used in the present investigation in order to obtain the quantitative dependence of the exchange rate on concentrations of both exchange reactants and hydrogen ion and on the temperature. It is assumed that I^{131} behaves chemically[3] as does I^{127}.

The iodine–iodate exchange, with the exchange rate R, may be studied by the use of the radioactive I^{131} tracer

$$\mathrm{II}^{131} + \mathrm{IO_3}^- = \mathrm{II} + \mathrm{I}^{131}\mathrm{O_3}^-$$

The exchange rate, a function of the total concentrations and temperature, follows the general law for a first order reversible reaction, given by[4]

$$R = \frac{2\{\mathrm{I_2}\}\{\mathrm{IO_3}^-\}}{2\{\mathrm{I_2}\} + \{\mathrm{IO_3}^-\}}\,\frac{\ln 2}{T_{1/2}}$$

The braces are used to denote formal concentrations expressed in gram-formula weights of the enclosed species per liter of solution, and $T_{1/2}$ represents the time required for the exchange to proceed half of the way to equilibrium. At complete exchange the specific activities of both reactants will be identical. A graph of log (1 − fraction exchange) against time will give a straight line from which the value of the "half-time" may be obtained.

If a single exchange path is operative, then by varying the concentrations of the reactants in separate experiments one can evaluate the order of the mechanism. At a given temperature R will be given by

$$R = k_T\,(\mathrm{I_2})^m(\mathrm{IO_3}^-)^n(\mathrm{H}^+)^p\Gamma$$

where parentheses are used to indicate actual concentrations of a particular species in moles or gram-ions per liter, and Γ includes the activity coefficients of the reactants and the transition state raised to the appropriate powers. We shall distinguish between actual concentrations of a species and formal concentrations expressed in gram-formula weights per liter of solution.

The activity of iodic acid can be held at a constant value for a series of experiments at constant temperature. Then from a determination of the exchange rate at various iodine concentrations a plot of log R *vs.* log $(\mathrm{I_2})$ will yield a straight line with a slope equal to the iodine dependence m. The use of iodine concentrations is permissible because the activity coefficient for this neutral species is approximately constant over the range of concentrations used. If there is in this concentration range an alternate path involving a different value of m the slope of log R *vs.* log $(\mathrm{I_2})$ will not be constant. We have attempted to evaluate m, n and p, the orders of the exchange reaction with respect to iodine, iodate ion and hydrogen ion.

---

[1] The material herein presented constitutes a part of the Ph.D. thesis of O. E. Myers, Monsanto Fellow, Washington University, June, 1949. Present address of Mr. Myers is Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[2] Hull, Shiflett and Lind, THIS JOURNAL, **58**, 535 (1936); Polessitsky, *Compt. rend. acad. sci., U. R. S. S.*, **24**, 540 (1939); Cottin and Haïssinsky, *Compt. rend.*, **224**, 1536 (1947).

[3] According to partition function calculations by Urey, *J. Chem. Soc.*, 562 (1947), we may expect equilibrium constants differing by only about 0.5% for these two isotopes in the iodine–iodate equilibrium.

[4] McKay, *Nature*, **142**, 997 (1938); Duffield and Calvin, THIS JOURNAL, **68**, 557 (1946); Friedlander and Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, New York, N. Y., 1949.

Experimental

Materials.—Radioiodine, I^{131}, "carrier-free" was obtained from the Oak Ridge National Laboratories on allocation from the Atomic Energy Commission. The experimentally observed half-life was 8.0 days; the aluminum half-thickness was 21.4 mg./sq. cm.; these compare favorably with the reported values, 8.0 *d.* and 23.0 mg./sq. cm. Al.[5]

Analytical reagent grade materials were used without further purification with the following exceptions. The perchloric acid (obtained from the G. Frederick Smith Co.) was doubly distilled. Sodium perchlorate for use in runs 16, 62–64 was prepared by neutralization of sodium hydroxide by this acid. Sodium iodate had to be recrystallized from hot aqueous solutions to obtain a product free from a basic impurity. For runs in which stopcock grease was required, Apiezon N grease was used.

Apparatus.—Runs at 25° were held to constant temperature to within 0.05° (as measured with a Bureau of Standards certified thermometer). Runs 8–10, 50–52 were kept in a covered oil-bath, at constant temperature ±0.2°. Other higher temperature runs were held constant to within ±0.05°. Runs at 0° were carried out in a Dewar flask packed with ice.

Where beta analysis was used the runs were made in retested 25.00-ml. volumetric flasks. The other runs were prepared in these flasks and aliquots were then sealed in 3-ml. Pyrex tubes.

Ethanol–argon-filled thin-window Geiger tubes were used for both beta and gamma measurements.

Preparation.—Labelled iodine was prepared in the reaction vessel by the oxidation of a known quantity of standard iodide solution. The calculated amount of iodide solution (sodium iodide for runs 1–4, 6–11, 24–27, 39, 41, 46, 52, 65–68, hydroiodic for the remainder except runs 13, 31–37) was admitted from a calibrated buret into the volumetric flask, and the tracer solution was added. Other reagents (such as sodium iodate or perchloric acid) were then admitted in the same way, and the contents cooled to 20°. The desired amount of standard iodic acid solution (including that required for oxidation of the iodide) was now added. The flask was then filled with distilled water to 25.00 ml., stoppered, shaken and placed in the thermostat. This procedure was modified in that standard labelled iodine solution was added in runs 13, 31–37.

Approximately one hundred times as much tracer (about 25 μc. each) was used in runs where the analysis was by means of gamma radiation. In these runs the reaction mixture was quickly divided into several 2.0-ml. portions which were sealed in glass ampules and placed in the thermostat. In this way the volatilization of iodine and its possible reaction with stopcock grease were minimized. It was possible by this technique to measure with greater precision the dependence of the exchange rate on temperature.

Beta Analysis.—(Runs 1–13, 24–27, 31–42, 46–55, 58–61, 65–68, 75, 77, 79, 80, 82–87, 93, 110–112.) In general, 0.5-ml. samples were transferred from the volumetric flask to a 3-ml. centrifuge cone by means of a capillary pipet, and extracted with three portions of about 0.5 ml. each of the organic solvent, carbon tetrachloride or benzene. (Where necessary the reaction was first quenched by dilution with water.) Mixing of the two phases was accomplished by vigorous stirring with a platinum wire. After a short centrifugation the organic phase was drawn off by means of a second capillary pipet and added to a second 3-ml. cone containing 0.5 ml. 0.055 *f* sodium iodide and one drop of 0.05 *f* sodium bisulfite. The sodium iodide content of this solution was adjusted to give the desired resultant weight per unit area when prepared for counting. Second and third extractions were made and combined with the first. The efficiency of the separation procedure was tested to show that less than 0.1% of the iodine activity remained in the aqueous phase and that less than 0.2% of the iodate activity was extracted.

The iodine fraction after reduction by the bisulfite solution was centrifuged, and the aqueous solution was withdrawn and placed on a 22-mm. microscope cover glass. At this time a 5% excess of silver nitrate solution was added.

The iodate fractions for most of these runs were mounted by evaporation directly on cover glasses. All mountings had an average thickness of 2.3 mg./sq. cm. (inactive iodic acid was added when necessary). In runs 12, 13, 53–55, 58–61, 75, 82–84 and 93 the iodate was precipitated as silver iodate, washed and dissolved in ammonium hydroxide; this solution was then transferred to the cover glass. Both methods ordinarily gave results identical to those obtained by reduction of the iodate to iodide and preparation of the sample for counting as silver iodide, although direct mounting was not so consistent as silver iodate or silver iodide mounting when perchloric acid was present.

All solutions on cover glasses were evaporated to dryness under an infrared lamp. When dry the glasses were mounted on cardboard and covered with moisture-resistant cellophane in preparation for the measurement of their (beta) radioactivities.

Gamma Analysis.—(Runs 14–23, 28–30, 43–45, 56, 57, 62–64, 69–74, 76, 78, 81, 88–92, 94–109, 113–128.) At a selected time an ampule was quickly cooled and placed in a reproducible position at the side of the counter tube; there its gamma radiation was measured. The tip of the ampule was then broken off and the iodine extracted with benzene as before. The ampule was then returned to its position near the counter tube, and the remaining gamma activity was measured. (At iodic acid concentrations greater than 0.2 *f* it was necessary to warm the solution in order to remove the iodine completely; this was done in the presence of benzene in a fourth extraction in order to minimize the error due to exchange at higher temperatures.)

Runs in 5.00 *f* perchloric acid were attempted but very poor exchange curves were obtained. These data were therefore largely disregarded.

Accuracy.—Wherever practical the statistical errors of radioassay were held to a standard deviation of two per cent. or less. Exchange half-times and rates are tabulated with uncertainties estimated from the extent of the standard deviation for each sample. Per cent. exchange has been calculated on the basis of the individual samples. Corrected radioactivity totals (radioactive material balances) generally agreed to within three per cent.

At least three samples were taken, at different times, for each run. In all cases (except as noted in 5.00 *f* perchloric acid, and where obvious heterogeneous exchange took place in runs 5′, 40′, 42′) the first order exchange law[4] was closely followed. Run 75 was performed with radioiodate rather than radioiodine in order to demonstrate further that no net chemical reaction occurs during the exchange. Also representative reaction mixtures were analyzed for iodine, iodate, and acidity after several weeks.

Duplicate results with low and high specific activities (*e. g.*, runs 2 and 3) verify that the exchange is not influenced by the intensity of the radioactivity. Variations in the surface to volume ratio (*e. g.*, runs 101 and 101′) showed that there is no obvious heterogeneous exchange at glass surfaces, at least at hydrogen ion concentrations as large as 1.00 *f*. Runs in comparative darkness (runs 8–10, 50–52) showed that photochemically induced exchange is not observable.

Experimental Results

Iodine Dependence.—From Fig. 1 and Table I it is seen that the order of the exchange reaction with respect to the concentration of iodine is 0.60 between 0 and 50° in iodic acid alone or in the presence of lithium iodate, sodium perchlorate or perchloric acid at concentrations as great as 1.00 *f*. All experiments which permit the determination of this dependence are listed in Table I, and representative data are plotted in Fig. 1.

---

[5] Livingood and Seaborg, *Phys. Rev.*, **54**, 775 (1938); Seaborg, Livingood and Kennedy, *ibid.*, **57**, 363 (1940).

TABLE I

IODINE DEPENDENCE

No.	Temp., °C.	$10^3\{I_2\}$	$\{HIO_3\}$	$\{NaIO_3\}$	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$	*m*[a]
1	25.0	1.00	0.098	0.002	317 ± 10	4.28	0.60 ± 0.04
2	25.0	0.70	.099	.001	288 ± 8	3.32	
3	25.0	.70	.099	.001	280 ± 4	3.41	
41	25.0	.50	.099	.001	249 ± 10	2.76	
42	25.0	.50	.100	...	262 ± 20	2.62	
39	25.0	.35	.099	.001	212 ± 6	2.28	
4	25.0	.25	.100	...	184 ± 6	1.87	
5	25.0	.25	.100	...	196 ± 8	1.76	
36	24.9	.22	.099	...	186 ± 8	1.66	
6	0	.70	.099	.001	5100 ± 300	0.187	.76 ± 0.16
7	0	.35	.099	.001	4400 ± 300	0.110	
8	35.0	.70	.099	.001	100 ± 3	9.56	.60 ± 0.08
9	35.0	.35	.099	.001	76.5 ± 2.0	6.30	
52	50.0	.70	.099	.001	22.4 ± 0.6	42.7	.58 ± 0.07
10	50.0	.35	.099	.001	16.9 ± 0.4	28.5	
38	25.0	.35	.020	...	26000 ± 3000	0.018	.35 ± 0.25
34	24.9	.11	.020	...	12500 ± 2000	.012	
45	25.0	1.00	.050	...	2420 ± 60	.551	.54 ± 0.05
11	25.0	0.70	.051	...	1900 ± 90	.497	
40	25.0	0.50	.050	...	1890 ± 90	.360	
35	24.9	0.11	.050	...	888 ± 9	.174	
47	24.9	1.00	.200	...	68.3 ± 3.4	20.4	.62 ± 0.08
43	25.0	0.50	.200	...	51.7 ± 0.3	13.3	
49	24.9	1.00	1.001	...	3.67 ± 0.22	377	.74 ± 0.10
44	25.0	0.50	1.000	...	3.06 ± 0.20	226	
54	50.0	1.00	0.020	...	2390 ± 70	0.527	.51 ± 0.10
50	50.0	0.70	.020	...	2060 ± 80	0.440	
55	50.0	1.00	.050	...	150 ± 3	8.86	.84 ± 0.20
51	50.0	0.70	.052	...	144 ± 7	6.57	
				$\{HClO_4\}$			
112	25.0	1.00	.020	0.200	1340 ± 30	0.942	.56 ± 0.07
109	25.0	0.50	.020	0.200	1032 ± 29	.640	
74	25.0	1.00	.001	1.000	1550 ± 90	.298	.53 ± 0.06
89	25.0	0.50	.001	1.000	1680 ± 40	.206	
80	24.9	1.00	.020	0.990	238 ± 10	5.29	.63 ± 0.06
81	25.0	1.00	.020	1.000	225 ± 4	5.60	
93	25.0	0.50	.020	0.990	181 ± 4	3.65	
12	25.0	0.25	.020	0.990	150 ± 3	2.26	
83	24.9	1.00	.100	0.990	43.8 ± 0.6	31.0	.63 ± 0.03
95	25.0	0.50	.100	1.000	34.1 ± 0.8	20.1	
98	50.0	1.00	.001	1.000	79.4 ± 3.4	5.82	.63 ± 0.04
103	50.0	0.50	.001	1.000	92.0 ± 2.7	3.77	
99	50.0	1.00	.002	1.000	65.2 ± 0.8	10.6	.56 ± 0.10
13	50.0	0.2	.002	1.000	54.0 ± 2.0	4.3	
125	25.0	0.50	.020	3.000	182 ± 3	3.62	1.12 ± 0.09
14	25.0	1.00	.020	3.000	160 ± 8	7.87	
				$\{LiIO_3\}$			
19	25.0	1.00	.020	1.000	1510 ± 50	0.916	0.62 ± 0.08
15	25.0	0.50	.020	1.000	1110 ± 18	0.594	
				$\{NaClO_4\}$			
16	25.0	0.7[b]	.100	2.000	690 ± 80	1.97	0.66 ± 0.44
63	25.0	0.50	.100	2.000	434 ± 12	1.58	

[a] From the slope of log *R* *vs.* log (I_2). [b] Performed in the presence of undissolved iodine. The solubility of iodine in this solution was found to be 0.0007 *f*.

In 3.00 or 5.00 *f* perchloric acid there is an indication of an increased iodine dependence. It has not been possible to determine the exact trend of this dependence because of the large uncertainties involved in the determination of exchange rates at these high acidities.

TABLE II

HYDROGEN ION DEPENDENCE

No.	Temp., °C.	$10^3\{I_2\}$	$\{LiIO_3\}$	$\{HIO_3\}$	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$	p[a]
17	0	0.58	1.000	0.020	20000 ± 2000	0.040	1.62 ± 0.21
18	0	0.58	1.000	.050	4560 ± 400	0.176	
19	25	1.00	1.000	.020	1510 ± 50	0.916	1.95 ± 0.06
20	25	1.00	1.000	.050	253 ± 4	5.47	
21	50	1.00	1.000	.010	392 ± 5	3.53	1.81 ± 0.03
22	50	1.00	1.000	.020	112 ± 3	12.3	
23	50	1.00	1.000	.050	21.0 ± 0.6	64.8	
19′	25	1.00	0.500	.020	1795 ± 30	0.769	
22′	50	1.00	.500	.020	130 ± 7	10.6	
24	25	0.96	.088[b]	.0083	21300 ± 1400	0.056	1.83 ± 0.05
25	25	1.00	.083[b]	.0118	12400 ± 1000	0.109	
26	25	0.96	.069[b]	.027	2650 ± 100	0.491	
27	25	0.99	.051[b]	.047	955 ± 36	1.40	
1	25	1.00	.002[b]	.098	317 ± 10	4.28	

[a] From the slope of log R *vs.* log $\{HIO_3\}$; *i. e.*, log R *vs.* log $\{H^+\}$. [b] Sodium iodate.

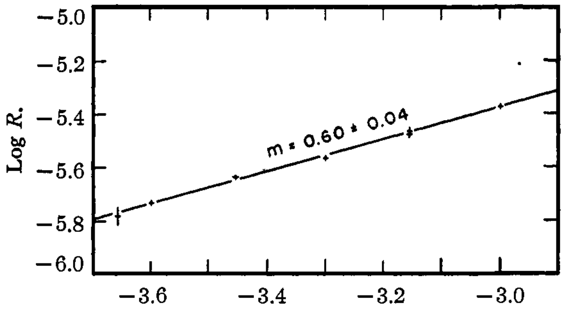

Fig. 1.—Iodine dependence: 0.010 *f* HIO_3, 25.0°.

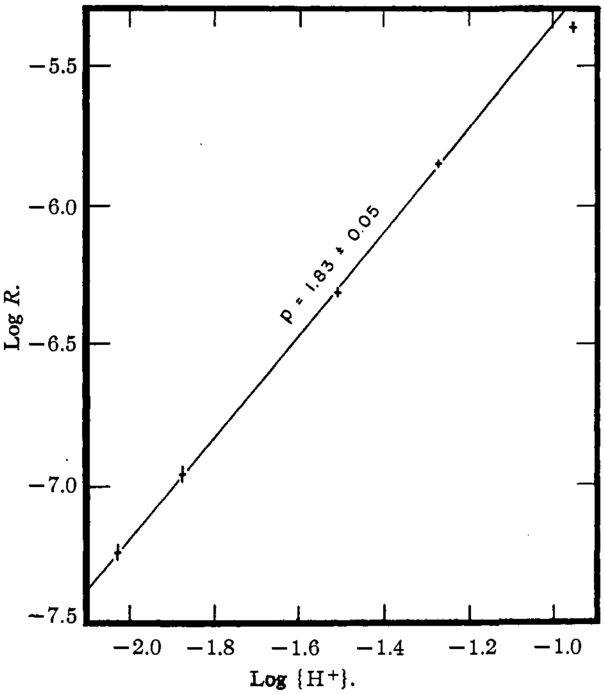

Fig. 2.—Hydrogen ion dependence: 0.100 *f* IO_3^-, 0.001 *f* I_2, 25.0°.

Hydrogen Ion Dependence.—In some runs 1.00 *f* lithium iodate was used to provide a nearly constant ionic strength for a determination of p, the order of the reaction with respect to hydrogen ion. From a graph of log R *vs.* log$\{H^+\}$, with the iodine concentration, iodate activity and temperature constant, we obtain as the best value p = 1.79 ± 0.08.

One series, at an ionic strength of 0.100 prepared by the addition of sodium iodate, led to a hydrogen ion dependence of 1.83 ± 0.05 on the basis of formal acid concentrations. Because iodic acid is not fully ionized, the amount of iodate ion held as undissociated acid should lead to an appreciable decrease in the exchange rate at the highest iodic acid concentration in this series. As shown in Fig. 2, the highest point falls somewhat below the line (p = 1.83 ± 0.05) through the other points.

Iodic Acid Dependence.—Figure 3A shows the result (corrected to an iodine concentration of 0.001 *f*) for all experiments in which only iodic acid and iodine were present in solution (Table III). The logarithm of the observed exchange rate is here plotted against the logarithm of the formal iodic acid concentration. A curve is obtained which appears to approach a line of slope about 3.6 at the lowest iodic acid concentrations; the curvature at other concentrations is to be attributed to the presence of undissociated iodic acid. Following Randall and Allen[6] we may define the activity coefficient of iodic acid as $\gamma = \alpha\gamma_{\pm}$, where α is the degree of ionization and is the $\gamma_{\pm}$ mean activity coefficient of the ions. If the values of $\alpha\gamma_{\pm}$ from freezing point data[7] are used to correlate the exchange data, consistent results are obtained. This is shown in Figs. 3B and 3C, where we plot as abscissa log $\alpha\gamma_{\pm}\{HIO_3\}$ instead of log $\{HIO_3\}$. Between 0.01 and 1.00 *f*

---

(6) Randall and Allen, THIS JOURNAL, **52**, 1814 (1930).

(7) Abel, Redlich and Hersch, *Z. physik. Chem.*, **A170**, 112 (1934); Groschuff, *Z. anorg. Chem.*, **47**, 331 (1905).

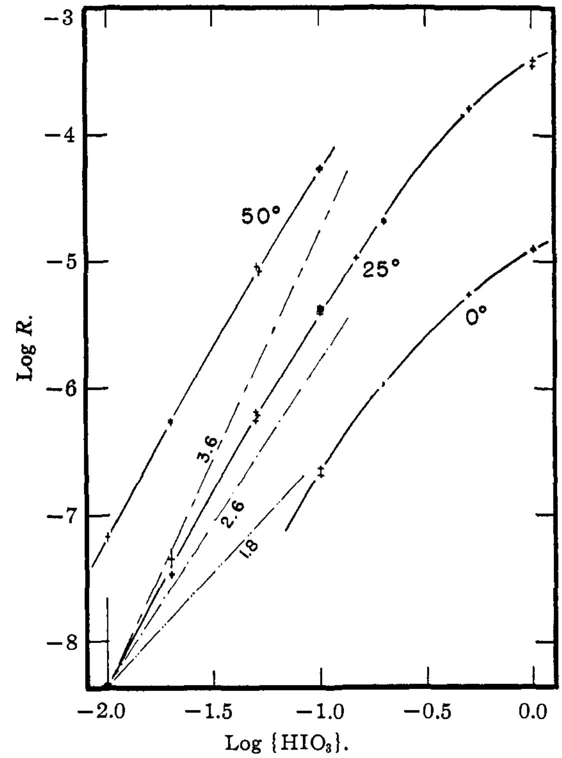

Fig. 3A.—Iodic acid dependence: corrected to 0.001 *f* I_2.

iodic acid the exchange rate varies with the iodic acid activity raised to the 3.65 ± 0.14 power. Since

$$\alpha\gamma_{\pm}\{\mathrm{HIO_3}\} = \sqrt{\gamma_{\pm}^2\,(\mathrm{H^+})(\mathrm{IO_3^-})} \qquad (1)$$

if $(\mathrm{H^+}) = (\mathrm{IO_3^-})$

$$\alpha\gamma_{\pm}\{\mathrm{HIO_3}\} = \sqrt{\gamma_{\pm}^2(\mathrm{IO_3^-})^2} = \gamma_{\pm}(\mathrm{IO_3^-}) \qquad (2)$$

$$R = k_{\mathrm{T}}(\mathrm{I_2})^m(\mathrm{IO_3^-})^{n+p}\gamma^{n+p}/\gamma_{\mathrm{c}} \qquad (3)$$

$$R = \frac{k_{\mathrm{T}}}{\gamma_{\mathrm{c}}}(\mathrm{I_2})^m(\alpha\gamma_{\pm}\{\mathrm{HIO_3}\})^{n+p} \qquad (4)$$

Thus

$$\left(\frac{\partial \log R}{\partial \log \alpha\gamma_{\pm}\{\mathrm{HIO_3}\}}\right)_{(\mathrm{I_2}),T,\gamma_{\mathrm{c}}} = n + p = 3.6 \qquad (5)$$

We may notice that when $n = p$, as appears to be the case here, we can derive Eq. 5 without the assumption $(\mathrm{H^+}) = (\mathrm{IO_3^-})$.

The rate law appears to involve equal numbers of positive and negative ions so that the critical complex[8] is thought to be neutral, therefore the departure of its activity coefficient γ_{c} from unity should be negligible. Figure 3B also shows the curves which would have been expected to result if one less ion, either hydrogen or iodate, entered the transition state (slope ~2.6), or if one more ion were involved (slope ~4.6). These lines are based on assumed equality of the hydrogen and iodate ion activities, and are very slightly curved to take account of the estimated effect of the activity coefficient of a singly charged transition state.

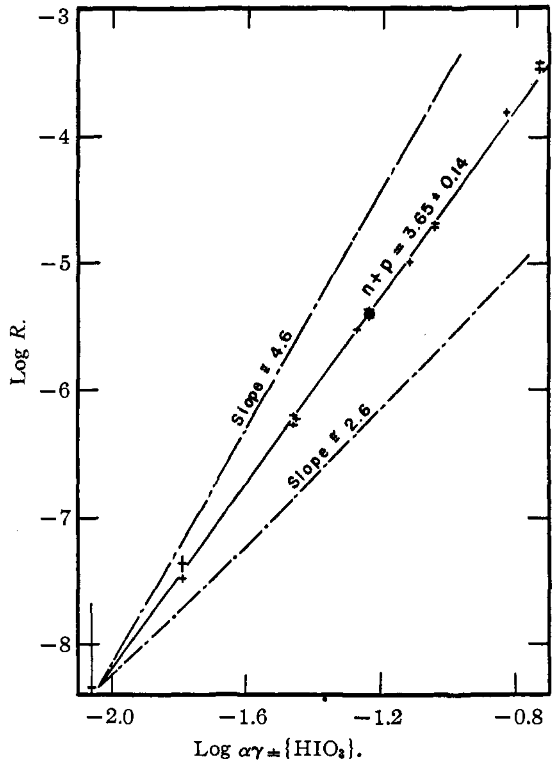

Fig. 3B.—Iodic acid activity dependence at 25°.

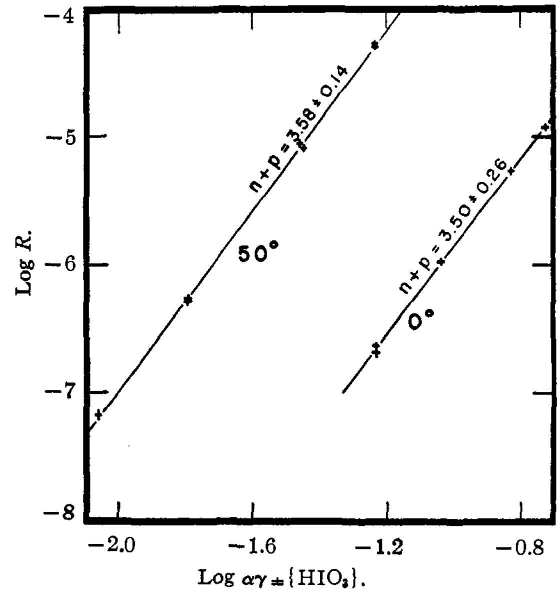

Fig. 3C.—Iodic acid activity dependence at 0° and 50°.

It should be pointed out that the product $\gamma_{\pm}^2(\mathrm{H^+})(\mathrm{IO_3^-}) = (\alpha\gamma_{\pm}\{\mathrm{HIO_3}\})^2$ from the Randall and Allen treatment[6] is relatively independent of polymerization equilibria which may be present in this case.

Iodate Ion Dependence.—Taking the iodic acid dependence equal to 3.6 we see that the iodate ion dependence *n* must be equal to the

---

[8] Brønsted, *Z. physik. Chem.*, **102**, 169 (1922).

TABLE III

IODIC ACID DEPENDENCE

No.	Temp. °C.	$10^3\{I_2\}$	$\{HIO_3\}$	$\alpha\gamma_\pm$[a]	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$
28	0	0.50	0.200	0.459	1036 ± 25	0.680
29	0	.50	0.500	.295	196 ± 6	3.53
30	0	.50	1.000	.186	86 ± 3	8.05
31	24.9	.11	0.001	.965	$>2.8 \times 10^4$	<0.0045
32	24.9	.11	.005	.907	$>2.0 \times 10^4$	<0.0075
33	24.9	.11	.010	.866	34000 ± 9000	0.0044
34	24.9	.11	.020	.806	12500 ± 2000	0.012
35	24.9	.11	.050	.691	888 ± 9	0.174
36	24.9	.22	.099	.581	186 ± 8	1.66
37	24.9	.22	.149	.510	74.3 ± 3.1	4.17
38	25.0	.35	.020	.806	26000 ± 3000	0.018
39	25.0	.35	.099	.581	212 ± 6	2.28
40	25.0	.50	.050	.691	1890 ± 90	0.360
41	25.0	.50	.099	.581	249 ± 10	2.76
42	25.0	.50	.100	.581	262 ± 20	2.62
43	25.0	.50	.200	.459	51.7 ± 0.3	13.3
44	25.0	.50	1.000	.186	3.06 ± 0.20	226
45	25.0	1.00	0.050	.691	2420 ± 50	0.551
46	25.0	1.00	.088	.602	449 ± 10	3.02
1	25.0	1.00	.098	.581	317 ± 10	4.28
47	24.9	1.00	.200	.459	68.3 ± 3.4	20.4
48	24.9	1.00	.500	.295	8.67 ± 0.14	159
49	24.9	1.00	1.001	.186	3.67 ± 0.22	377
50	50.0	0.70	0.020	.806	2060 ± 80	0.440
51	50.0	0.70	.052	.687	144 ± 7	6.57
52	50.0	0.70	.100	.581	22.4 ± 0.6	42.7
53	50.0	1.00	.010	.866	18700 ± 1400	0.067
54	50.0	1.00	.020	.806	2390 ± 70	0.527
55	50.0	1.00	.050	.692	151 ± 3	8.86
56[b]	25.0	1.00	.100	....	350 ± 20	3.88
57[b]	25.0	1.00	.200	....	67.3 ± 3.1	20.4
				$\{NaClO_4\}$		
58	25.0	1.00	.050	0.154	3400 ± 200	0.392
59	25.0	1.00	.100	0.117	462 ± 13	2.94
60	25.0	1.00	.100	0.122[c]	339 ± 9	4.01
61	25.0	1.00	.200	0.053	68.3 ± 0.7	20.1
62	25.0	0.50	.050	2.000	3050 ± 140	0.223
63	25.0	0.50	.100	2.000	434 ± 12	1.58
64	25.0	0.50	.200	2.000	70.8 ± 3.1	9.74

[a] The effect of temperature on the activity coefficient of iodic acid is not known. The tabulated values are those at the freezing point for weight-formal solutions. [b] These runs contained 20 volume % ethanol. [c] Formal concentration of added sodium nitrate.

hydrogen ion dependence; $n = p = 1.8$. Also, we can see from the observed iodine dependence $m = 0.6$ that 1.2 iodine atoms enter the transition state; since this must be an integral number when all iodine species are considered, the possible values of n are limited to integral numbers minus 0.2, that is, to values like -0.2, 0.8, 1.8, etc.

In an early attempt to obtain a direct determination of the order n with respect to iodate ion sodium iodate was added to 0.1 f HIO_3 (Table IVA). A plot of log R *vs.* log$\{IO_3^-\}$ is of course a curve because of the variation of hydrogen ion activity. The initial slope at the lower concentrations (where the change in concentration of undissociated acid is relatively small) is roughly 1.5. An attempt was made to correct for the resultant decrease in actual hydrogen ion concentration when iodate was added by means of the iodic acid dissociation constant from conductivity measurements,[9] $K = 0.16$ at 25°, and an estimate of the mean activity coefficient of the ions. Values of n between 1.5 and 2.0 can be obtained.

TABLE IVA

IODATE ION DEPENDENCE, 0.001 f I_2, 25.0°

No.	$\{HIO_3\}$	$\{NaIO_3\}$	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$
1	0.098	0.002	317 ± 10	4.28 ± 0.14
65	.098	.052	181 ± 7	7.55 ± 0.30
66	.098	.154	118 ± 5	11.5 ± 0.5
67	.098	.252	104 ± 7	13.2 ± 0.9
68	.098	.401	82 ± 5	16.8 ± 1.0

An alternative approach to the direct determination of the iodate ion dependence is to perform a series of experiments at constant ionic strength in a large excess of a strong acid. Insofar as no appreciable polymerization phenomena occur, the true iodate ion concentration would then be proportional to its formal concentration, the hydrogen ion concentration would be invariant, and the activity coefficients should all remain essentially constant. Several exchange series were performed at chosen concentrations of perchloric acid (Tables IVB and IVC); nitric acid was used in

TABLE IVB

IODATE ION DEPENDENCE IN 1.00 f $HClO_4$

No.	Temp., °C.	$10^3\{I_2\}$	$\{HIO_3\}$	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$
69	0	0.65	0.020	4560 ± 300	0.186 ± 0.012
70	0	.65	.050	1670 ± 35	0.526 ± 0.011
71	0	.50	.050	1597 ± 26	0.425 ± 0.006
72	0	.50	.100	817 ± 17	0.839 ± 0.018
73	0	.50	.200	394 ± 17	1.75 ± 0.08
74	25.0	1.00	.001	1550 ± 90	0.298 ± 0.016
75[a,b]	24.9	1.1	.002	1140 ± 80	0.636 ± 0.041
76	25.0	1.00	.002	1204 ± 36	0.575 ± 0.017
77[a]	24.9	1.00	.007	631 ± 40	1.71 ± 0.10
78	25.0	1.00	.007	564 ± 9	1.91 ± 0.03
79[a]	24.9	1.00	.012	387 ± 20	3.06 ± 0.16
80[a]	24.9	1.00	.020	238 ± 10	5.29 ± 0.22
81	25.0	1.00	.020	225 ± 4	5.60 ± 0.10
82[a]	24.9	1.00	.040	112 ± 2	11.3 ± 0.3
83[a]	24.9	1.00	.100	43.8 ± 0.6	31.0 ± 0.5
84[a]	24.9	1.00	.200[c]	22.1 ± 0.4	62.1 ± 1.2
85[d]	24.9	1.00	.007	534 ± 18	2.02 ± 0.07
86[d]	24.9	1.00	.012	353 ± 8	3.37 ± 0.08
87[d]	24.9	1.00	.020	212 ± 6	5.95 ± 0.17
88	25.0	0.50	.0005	2070 ± 130	0.112 ± 0.007
89	25.0	.50	.001	1680 ± 90	0.206 ± 0.006
90	25.0	.50	.002	1140 ± 20	0.406 ± 0.008
91	25.0	.50	.005	661 ± 6	0.875 ± 0.008
92	25.0	.50	.010	370 ± 2	1.703 ± 0.009
93[a]	25.0	.50	.020	181 ± 4	3.65 ± 0.10
94	25.0	.50	.050	72.4 ± 0.4	9.38 ± 0.05
95	25.0	.50	.100	34.1 ± 0.8	20.1 ± 0.1
96	25.0	.50	.125	26.2 ± 0.4	26.3 ± 0.4
97	25.0	.50	.500	7.10 ± 0.30	97.4 ± 4.0
98	50.0	1.00	.001	79.4 ± 3.4	5.82 ± 0.24
99	50.0	1.00	.002	65.2 ± 0.8	10.6 ± 0.1
100	50.0	1.00	.007	39.6 ± 0.5	27.2 ± 0.5
101	50.0	1.00	.020	15.7 ± 0.1	80.4 ± 0.6
101′	50.0	1.00	.020	15.7 ± 0.2	80.4 ± 1.2
102	50.0	0.50	.0005	112.0 ± 2.0	2.06 ± 0.04
103	50.0	.50	.001	90.6 ± 2.7	3.83 ± 0.11
104	50.0	.50	.002	73.9 ± 1.4	6.25 ± 0.11
105	50.0	.50	.005	42.9 ± 0.8	13.5 ± 0.3
106	50.0	.50	.010	24.8 ± 0.3	25.4 ± 0.3

[a] 0.990 f perchloric acid. [b] Initially radioiodate. [c] Formal concentration of added sodium iodate. [d] 1.000 nitric acid rather than perchloric acid.

---

(9) Fuoss and Kraus, This Journal, **55**, 476 (1933); Fuoss and Shedlovsky, *ibid.*, **71**, 1496 (1949).

TABLE IVC

IODATE ION DEPENDENCE IN PERCHLORIC ACID, 25.0°

No.	$10^3\{I_2\}$	$\{HIO_3\}$	$\{HClO_4\}$	$T_{1/2}$, hr.	$10^6 R$, hr.$^{-1}$
107	0.50	0.005	0.200	5450 ± 400	0.106 ± 0.008
108	0.50	.010	.200	2530 ± 100	.249 ± 0.009
109	0.50	.020	.200	1032 ± 29	.630 ± 0.018
110	1.00	.007	.200	5280 ± 200	.204 ± 0.080
111	1.00	.012	.200	2585 ± 100	.459 ± 0.017
112	1.00	.020	.200	1340 ± 30	.942 ± 0.022
113	0.50	.005	.500	1460 ± 120	.395 ± 0.035
114	.50	.010	.500	738 ± 24	.854 ± 0.028
115	.50	.020	.500	376 ± 11	1.75 ± 0.05
116	.50	.050	.500	117 ± 3	5.80 ± 0.14
117	.50	.002	2.000	463 ± 25	0.998 ± 0.050
118	.50	.005	2.000	327 ± 6	1.76 ± 0.03
119	.50	.010	2.000	206 ± 3	3.06 ± 0.04
120	.50	.020	2.000	126 ± 2	5.23 ± 0.09
121	.50	.050	2.000	62.0 ± 2.5	10.94 ± 0.42
122	.50	.002	3.000	542 ± 40	0.852 ± 0.070
123	.50	.005	3.000	360 ± 9	1.60 ± 0.05
124	.50	.010	3.000	257 ± 11	2.45 ± 0.10
125	.50	.020	3.000	182 ± 3	3.62 ± 0.06
126	.50	.050	3.000	97.2 ± 1.4	6.98 ± 0.10

one series at unit ionic strength (Table IVB). It was found that the apparent iodate ion dependence, ($\partial \log R/\partial \log \{IO_3^-\}$), decreases from about 1.5 at 0.20 *f* to roughly 0.65 at 3.00 *f* perchloric acid. In nitric or sulfuric acid[10] the iodate dependence is nearly the same as in the corresponding series with perchloric acid, although for a given formal iodic acid concentration the exchange rate is greater in these acids.

Figure 4A shows a graph of log *R* *vs.* log $\{IO_3^-\}$ for the extended series at 1.00 *f* perchloric acid and 25°. The resulting line appears to have a real curvature. Its slope is 0.83 ± 0.10 between 0.0005 and 0.001 *f* and 1.14 ± 0.06 between 0.05 and 0.10 *f* iodate ion.

For the exchange path in the absence of perchloric acid we have seen that the dependence of the rate on iodate ion is the same as on hydrogen ion, $n = p = 1.8$. Therefore, provided the various activity coefficients are about the same at the same ionic strength, the exchange rate due to this particular path should be about the same either in 1 *f* perchloric acid at a given formal iodate concentration or in 1 *f* lithium iodate with the same given hydrogen ion concentration. We refer to a pair of otherwise identical exchange runs with hydrogen ion and iodate ion formal concentrations just reversed as "mirror images." A comparison of the runs shown in Fig. 4A with their "mirror image" series (runs 19 and 20) shows that at low iodate concentrations in perchloric acid the rate is several times faster than would correspond to the exchange path found in the absence of perchloric acid. The best line of slope 1.8 estimated from the "mirror image" series is plotted in Fig. 4A. The differences between the observed values of *R* and the corresponding values of *R* from the "mirror image" line form a line of slope 0.8, within the limits of experimental error, extending from the lowest iodate concentration tested to about 0.1 *f*. The solid curve of Fig. 4A is actually the sum of these two component lines. This treatment is confirmed by the series in 1.00 *f* perchloric acid at 50° ("mirror image" series of runs 21–23), and at 0° (when compared with runs 17, 18), although the activation energy of the 0.8 component is considerably greater than that of the 1.8 component.

Further evidence that the exchange rate in strong acid is a composite of these two orders with respect to iodate ion may be obtained from a comparison of the series in 0.50 *f* perchloric acid (runs 113–116) with runs 68 and 19, or by comparison of the series in 0.20 *f* perchloric acid (runs 107–112) with a mirror image series obtained by interpolation from the series of runs 1, 65–68. The relative importance of the two orders is markedly different for these three concentrations of perchloric acid, yet the apparent iodate ion dependence may in every case be compounded from the mirror image line of slope 1.8 and a second straight line of slope

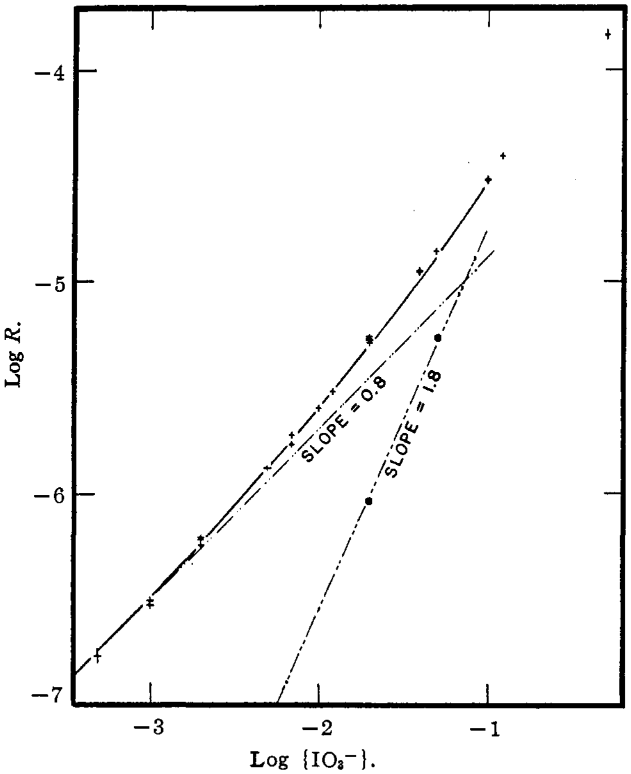

Fig. 4A.—Iodate ion dependence in 1.00 *f* $HClO_4$ at 25.0°, corrected to 0.001 *f* I_2: circles are determinations in the "mirror image" series (runs 19 and 20).

---

[10] J. W. Kennedy, unpublished work.

0.8. These results are shown in Figs. 4B and 4C.

In 2.00, 3.00 and 5.00 f perchloric acid the slope of the log R vs. log$\{IO_3^-\}$ curve seems to be less than 0.8 at low formal iodate ion concentrations.

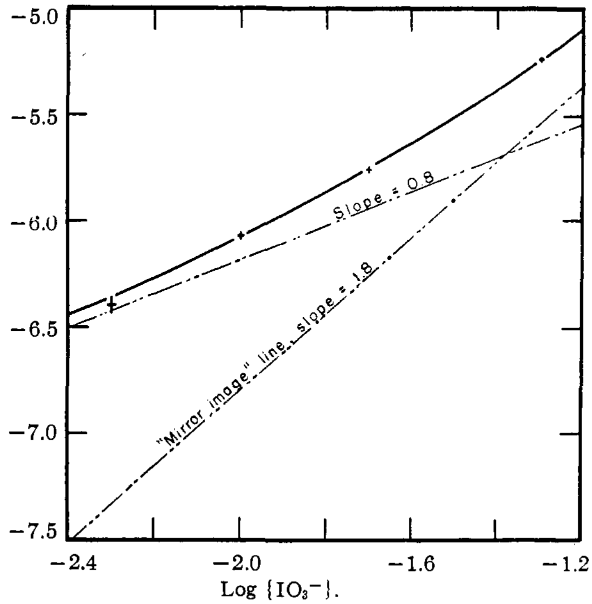

Fig. 4B.—Iodate ion dependence in 0.50 f $HClO_4$ at 25.0° and 0.0005 f I_2.

In part this effect may be attributed to some form of iodate ion polymerization, which may become increasingly important at high acidities. In this higher acidity range we have not been able to avoid some serious experimental errors, so that values much below 0.8 may not be real. We cannot exclude the possibility of the existence of a third, lower order with respect to iodate ion in the more concentrated acid.

Perchlorate Ion Dependence.—Some information may be obtained from the three series in 0.2, 0.5 and 1.0 f perchloric acid which would indicate that that portion of the exchange rate which is dependent upon the 0.8 power of iodate ion concentration does also depend on the perchlorate ion concentration. The two component rates have the same iodine dependence. If they have the same hydrogen ion dependence (a guess), we obtain the relation

$$R'/R'' = c[\gamma_-'(\mathrm{ClO_4^-})]^q/\gamma_-''(\mathrm{IO_3^-})$$

in which R' and R'' refer to the rates of the two iodate ion dependences, 0.8 and 1.8, respectively, c is a constant, γ_-' and γ_-'' are the activity coefficients of the two negative ions, and q is the order with respect to perchlorate ion. If we assume that both negative ions have the same activity coefficient or that their ratio is independent of the ionic strength, we obtain the table of values below, computed for $\{IO_3^-\} = 0.020 f$. It is not possible at the present time to obtain accurate information concerning the actual negative ion activities in these systems; c_a is the value of c calculated on the basis of $q = 1.0$, $(IO_3^-) = \{IO_3^-\}$. This treatment clearly does not establish with certainty the order with respect to perchlorate ion, but it does strongly suggest some role for this ion in that exchange mechanism corresponding to $n = 0.8$, and we are led to the hypothesis that here the perchlorate ion dependence does not differ greatly from unity.

TABLE V

THE EFFECT OF PERCHLORATE ION

$\{HClO_4\}$	R'/R''	c_a
0.2	0.88	0.088
0.5	2.13	.085
1.0	4.73	.095

Salt Effect.—The effect on the exchange reaction rate of the neutral salt sodium perchlorate may be seen from a comparison of runs 58, 59, 61 with runs 45, 1, 47 (Table III). The addition of 0.117 mole of sodium perchlorate per liter causes a reduction of about 30% in the rate at 0.10 f iodic acid. We interpret this as due to the displacement of the iodic acid ionization equilibrium, so that at the higher ionic strength (μ *ca.* 0.2) the actual concentration of iodic acid is reduced and therefore the product of the H^+ and IO_3^- ion activities is reduced. Crude estimates of the magnitude of this effect are consistent with the rate reduction observed. At an ionic strength of 2.00 in sodium perchlorate (runs 16, 62–64) the observed reduction in rate is about 40% at 0.1 f and about 30% at 0.2 f iodic acid.

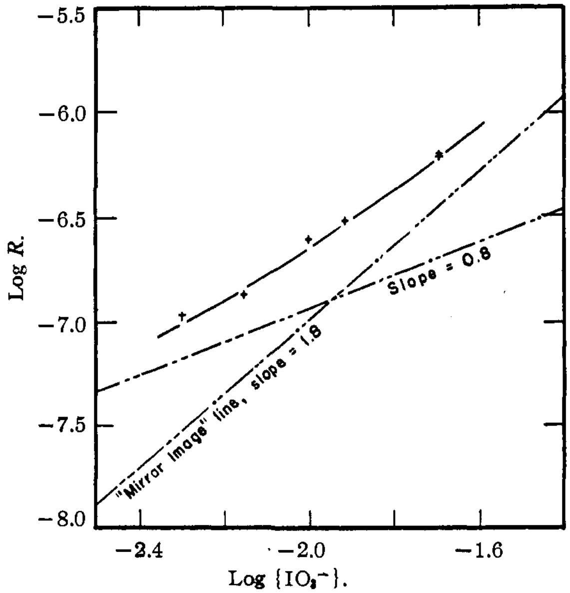

Fig. 4C.—Iodate ion dependence in 0.20 f $HClO_4$ at 25.0°, corrected to 0.0005 f I_2.

The effect of the displacement of the ionization equilibrium is to mask any effect of the neutral salt on the activity coefficient of the transition state, so that we may not expect from this information alone to distinguish between a neutral and a charged transition state. Where sodium nitrate had been added as a neutral salt (run 60) less rate reduction was observed than was caused by approximately the same concentration of sodium perchlorate (run 59).

Activation Energy.—In 1.00 *f* perchloric acid and at iodate ion concentrations sufficiently low so that the iodate ion activity is proportional to the formal concentration, the experimental activation energy is 22.4 ± 0.7 kcal. mole^{-1} for the exchange path of iodate order 0.8 and 19.5 ± 0.6 kcal. mole^{-1} for the exchange path of higher iodate order.

In iodic acid solutions the ionic strength was not constant and the actual concentrations of the exchange reactants could not be directly measured. Under these conditions the experimental activation energy was expected to be slightly dependent upon the formal concentration of iodic acid. The observed values are between 19.0 and 21.6 kcal. mole^{-1} in iodic acid solution or in the presence of excess iodate ion. These data may be found in the previous tables.

Discussion

The Sixth Order Law.—At 25° in aqueous solutions containing only iodic acid and iodine the exchange rate law may be represented by the following equation, where units of concentration and time are moles per liter and hours, respectively

$$R_{298.1} = (7.40 \pm 0.25)\gamma^{3.6}_{\pm(\mathrm{HIO_3})}(\mathrm{I_2})^{0.6}(\mathrm{IO_3^-})^{1.8}(\mathrm{H^+})^{1.8}$$

In the presence of negative ions other than iodate (*i. e.*, perchlorate, nitrate or sulfate, represented by X$^-$) it is possible that there is an additional term of the form

$$R' = k'\gamma^{1.6}_{\pm(\mathrm{HIO_3})}\gamma^{2.0}_{\pm(\mathrm{HX})}(\mathrm{I_2})^{0.6}(\mathrm{IO_3^-})^{0.8}(\mathrm{H^+})^{1.8}(\mathrm{X^-})$$

in which k' has been found for the anions named to be approximately one-tenth or one-hundredth as large as the rate constant involving an additional power of iodate ion. The value of k' for the case $\mathrm{X^-} = \mathrm{ClO_4^-}$ may be estimated crudely from the values of the hydrogen and iodate ion activity product from potential measurements of the iodine–iodate electrode in strong acid[11] and from the mean activity coefficient of perchloric acid.[12] The rough value obtained in this way is

$$k' = 0.15 \text{ liter}^{3.2} \text{ mole}^{-3.2} \text{ hr.}^{-1} \text{ for } \mathrm{X^-} = \mathrm{ClO_4^-}$$

The experimental conditions of the exchange reactions correspond to those of an equilibrium between iodide and excess iodate ions in acid solution

$$5\mathrm{I^-} + \mathrm{IO_3^-} + 6\mathrm{H^+} = 3\mathrm{I_2} + 3\mathrm{H_2O};\ \log K_{298.1} = 47.2 \pm 0.4^{13,14}$$

For most of our experiments the iodide concentration estimated from this equilibrium constant is of the order of 10^{-9} mole per liter. If we make the assumption that the exchange proceeds through the iodide–iodate reaction at equilibrium, solve the equilibrium constant expression for the activity of iodine, and substitute this into the equation for the exchange rate law, we find that the exponents emerge as integral numbers

$$R = [\gamma^2_{\pm(\mathrm{HI})}\gamma^2_{\pm(\mathrm{HIO_3})}/\gamma_c](\mathrm{I^-})(\mathrm{IO_3^-})(\mathrm{H^+})^3 \times [k_6\gamma^2_{\pm(\mathrm{HIO_3})}(\mathrm{IO_3^-}) + k_6'\gamma^2_{\pm(\mathrm{HX})}(\mathrm{X^-})]$$

This procedure is justified provided that the equilibrium concentrations of all intermediate species are very small compared to the formal concentrations of iodine and iodate, for in these circumstances the intermediates are built up to equilibrium concentrations before they can lead to any appreciable exchange. The rate constant k_6 is computed to be (5.7 ± 1.3) × 10^6 l.^{5} mole^{-5} sec.$^{-1}$ at 25°. When the additional negative ion is $\mathrm{ClO_4^-}$ k_6' is approximately 1.1 × 10^5 l.^{5} mole^{-5} sec.$^{-1}$ at 25°. (Apparently k_6' is somewhat greater for nitrate or sulfate ion.)

The Fourth Order Law.—Abel and Hilferding[15] have reported that at low iodide ion concentrations, of the order of 10^{-7} to 10^{-9} *f*, the iodide–iodate reaction follows a fourth order law

$$-\mathrm{d}(\mathrm{IO_3^-})/\mathrm{d}t = k_4(\mathrm{I^-})(\mathrm{IO_3^-})(\mathrm{H^+})^2$$

where k_4 = 405 liters^3 mole^{-3} sec.$^{-1}$ They maintained the low iodide ion concentration by shaking a large quantity of silver iodide with iodic acid solution. However, their data were analyzed with the simplifying assumption that iodic acid is fully ionized. When the appropriate activity coefficients of iodic acid are included in a treatment of these data the sixth order law (above) is more closely followed, and in none of the experiments in which even a rough comparison can be made does their observed reaction rate differ from that calculated by means of our sixth order law and rate constant by more than a factor of five. This degree of agreement we consider satisfactory in view of the fact that uncertainties in the ion activities are here raised to the sixth power.

The Fifth Order Law.—A fifth order rate law for the reaction between iodide and iodate at higher iodide concentrations has been reported by Dushman[16] and amended by Abel and Stadler[17]

$$-\mathrm{d}(\mathrm{IO_3^-})/\mathrm{d}t = k_5(\mathrm{I^-})^2(\mathrm{IO_3^-})(\mathrm{H^+})^2$$

with k_5 = 1.3 × 10^9 l.^{4} mole^{-4} sec.$^{-1}$ at 25°. We may extend our equilibrium exchange measurements to this region of higher iodide concentrations, but only in nearly neutral solutions so that the systems are not strictly comparable in their hydrogen ion concentrations. Run 127 in our exchange series was performed with 0.005 *f* sodium iodide and 0.100 *f* sodium iodate at 50° in nearly neutral solution. If the fifth order law of Abel and

---

(11) Sammet, *Z. physik. Chem.*, **53**, 665 (1905).

(12) Pearce and Nelson, THIS JOURNAL, **55**, 3075 (1933).

(13) Lundberg, Vestling and Ahlberg, *ibid.*, **59**, 264 (1937).

(14) "International Critical Tables," Vol. VII, p. 235.

(15) Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

(16) Dushman, *J. Phys. Chem.*, **8**, 453 (1904).

(17) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

Stadler is applicable the exchange half-time should have been very considerably less than 28,000 hours (we calculate 28,000 hours for 25°). Actually no measurable exchange was observed in any of five samples taken over a period of 1600 hr. From the estimated limits of counting error the exchange half-time was $> 5 \times 10^5$ hr. For exchange through the sixth order path we estimate that the half-time would be of the order of 10^{10} hours for these conditions. The observed fifth order law may possibly be related to the sixth order law with $X^- = I^-$.

The Exchange Mechanism.—We may speculate upon the reaction mechanism responsible for this sixth order rate law. A plausible one involves these rapid, reversible equilibria (where we represent associated ion pairs as A^+B^-)

$$H^+ + IO_3^- = HIO_3$$
$$HIO_3 + H^+ = IO_2^+ + H_2O$$
$$IO_2^+ + X^- = IO_2^+X^-$$
$$H^+ + I^- = H^+I^-$$

The possible formation of the ion IO_2^+ was suggested to us by the behavior of nitric acid, which has recently been shown[18,19] to form a reactive ion NO_2^+ especially in the presence of perchloric or sulfuric or other very strong acid. (It may be noted that iodic acid like nitric acid forms a double compound with concentrated perchloric or sulfuric acid.) The rate determining step might then be a two-electron transfer between the iodine species in the two ion pairs

$$IO_2^+X^- + H^+I^- = (H^+, I^-, IO_2^+, X^-) \longrightarrow HIO_2 + I^+X^-$$

It is presumed that these products would react rapidly with hydriodic acid to give iodine and water[20] (and X^- ion).

For experiments in which the apparent iodate dependence is 1.8 (*i. e.*, $X^- = IO_3^-$) it is seen that two iodate ions must enter the transition state in some form. If one were not reduced (as suggested in the above mechanism) and, further, if it became equivalent at any stage to an iodine atom originally present as iodide, then the addition of labelled (radioactive) hydriodic acid to an excess of iodic acid should result immediately in labelled iodic acid. We carried out such experiments under a variety of conditions, and no activity was detected in the residual iodic acid; this shows that the pentavalent iodine retains its identity, if indeed the transition state does split off iodate ion in this case.

Summary

The experimentally observed rate law for the iodine–iodate exchange reaction has been determined to be $R = (I_2)^{0.6}(H^+)^{1.8}(IO_3^-)^{0.8}[k(IO_3^-) + k'(X^-)]\Gamma$, in which X^- may be perchlorate, nitrate or sulfate ion, and Γ indicates that the activity coefficients of reactants and transition states are to be introduced with the appropriate powers. At 25° k has the value (7.40 ± 0.25) $l.^{3.2}$ $mole^{-3.2}$ $hr.^{-1}$ and k' is roughly 0.15 $l.^{3.2}$ $mole^{-3.2}$ $hr.^{-1}$ for $X^- = ClO_4^-$. The activation energy is approximately 20 kcal. $mole^{-1}$.

The exchange mechanism is shown to be the reversible reaction between iodide and iodate ions at equilibrium. Therefore the rate law for that reaction at very low iodide concentration is $-d(IO_3^-)/dt = (I^-)(IO_3^-)(H^+)^3[k_6(IO_3^-) + k_6'(X^-)]\Gamma$, in which k_6 at 25° is $(5.7 \pm 1.3) \times 10^6$ $l.^5$ $mole^{-5}$ $sec.^{-1}$ and k_6' for $X^- = ClO_4^-$ is *ca.* 1.1×10^5 $l.^5$ $mole^{-5}$ $sec.^{-1}$ at 25°.

A possible reaction mechanism is proposed which involves as a rate determining step a two-electron transfer from a chemical species containing I^- to one containing IO_2^+.

ST. LOUIS, MISSOURI RECEIVED MAY 31, 1949

[18] Hughes, Ingold and Reed, *Nature*, **158**, 448 (1946).

[19] Ingold and co-workers, *ibid.*, **158**, 480 (1946).

[20] Bray, THIS JOURNAL, **52**, 3580 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE RUMFORD DIVISION OF HEYDEN CHEMICAL CORPORATION]

Structure and Properties of the Condensed Phosphates. V. Molecular Weights of the Polyphosphates from Viscosity Data

BY JOHN R. VAN WAZER*

According to the theory and data presented in the first three papers of this series,[1] sodium phosphate glasses in the composition range between $Na_2O \cdot P_2O_5$ and $2Na_2O \cdot P_2O_5$ consist of polyphosphates, the average molecular weight of which becomes very large as the Na_2O/P_2O_5 ratio approaches unity. Since intrinsic viscosity is a function of molecular weight, viscosity measurements in solutions which are concentrated with respect to a simple salt (in order to minimize the effect of the ionic charge of the phosphate) and dilute with respect to the phosphate, should serve as an additional independent check of the polyphosphate theory of structure. If this theory presents a reasonable picture of the situation, such viscosity measurements should be related to the molecular weights, obtained from end-group titrations, by the equation[2] which was developed to fit data on organic high polymers and should result in reasonable values for the characteristic constants in this equation.

---

* Present address, The Great Lakes Carbon Corporation, Morton Grove, Illinois.

[1] Van Wazer, THIS JOURNAL, **72**, 639, 644, 647 (1950).

[2] *E. g.*, Baker, Ford and Heiss, *ibid.*, **63**, 3316 (1941).