Application of the Iodide-ion-selective Electrode to a Kinetic Study of the Periodate–Iodide Reaction

By **Catherine Marques** and **Robert A. Hasty,*** Department of Chemistry, University of the Witwatersrand, Johannesburg

The kinetics of the reaction of periodate and iodide have been studied and the effect of ionic strength and pH determined. An iodide-ion-selective electrode has been used to measure the rate of disappearance of iodide. The rate equation is $-d[IO_4^-]/dt = (5.9 \pm 1)$ dm^3 mol^{-1} s^{-1} $[I^-][IO_4^-]$, in the pH range 3.51—5.31. No hydrogen-ion dependence of the rate has been observed, in contrast to earlier studies. Activation parameters for the reaction have been determined.

THE development of a periodate-ion-selective electrode [1] has provided a new tool with which to follow periodate reactions, one of the most useful techniques in organic analysis.[2] A reinvestigation of the periodate reaction with iodide was begun in order to use this reaction as a model system in an extension of the development of periodate sensors. Although halate and perhalate reactions have been the subject of classical studies, the complexity of the reacting systems places restrictions on the classical approach.

Indelli [3] applied a microtitration method using a polarised platinum electrode as an indicator in a recent study of the periodate reaction with iodide. The results of that study indicate a hydrogen-ion dependence of the rate. Rate expressions reported in earlier work [4—6] differ widely with respect to hydrogen-ion dependence.

In this study, the iodide-ion-selective electrode which has been used successfully in the application to dynamic systems [7] in general and to iodate reactions [8] in particular was applied to the study of the kinetics of the periodate reaction with iodide.

EXPERIMENTAL

An integrated form of the rate expression was used to evaluate the rate constant for each specific solution. The iodide-ion concentration was used to follow the extent of the reaction and was determined potentiometrically with an Orion iodide-ion-selective electrode, model 94-53, and a double-junction saturated calomel reference electrode. An Orion combination pH electrode, model 91-05, was used for pH measurements. Potentials were measured to 0.1 mV on a Metrohm potentiometer, model E510, and recorded with respect to time on a Perkin-Elmer chart recorder, model 56.

A 100-cm^3 three-necked round-bottom flask was used as the reaction vessel. A teflon coated stirring bar driven by an air-powered stirrer, positioned below the reaction vessel, was used. The reaction vessel and stirrer were immersed in a thermostatted water bath which was controlled to within ±0.1° C. Analytical grade potassium iodide, sodium periodate, sodium acetate, acetic acid, and sodium nitrate were used to prepare stock solutions from which working solutions were prepared. The periodate solution was protected from light during storage.

A 50-cm^3 portion of a working solution having a particular pH and ionic strength was pipetted into the reaction vessel. Several aliquots of a potassium iodide solution were added after thermal equilibrium had been attained in order to establish a calibration curve for the potential against iodide-ion concentration in the system. Nernstian behaviour was observed at the three temperatures studied. The reaction was initiated by the rapid introduction of a 0.050 0 mol dm^{-3} sodium periodate solution in a pipette calibrated for delivery of a specified volume of solution. The potential against time response was recorded on the 20-mV expanded potential range of the recorder.

The iodide-ion-selective electrode provides a useful means of monitoring the iodide-ion concentration in a reacting system [7] as it is both selective and exhibits rapid response.[9] The selectivity coefficients for IO_4^- and IO_3^- were determined by a graphical method [10] to be $(5.0 \pm 0.3) \times 10^{-3}$ and $(2.0 \pm 0.1) \times 10^{-3}$ respectively, over an iodide activity range of 4.03×10^{-4}—6.00×10^{-4} mol dm^{-3} at a pH of 13 where the reaction of iodide with either periodate or iodate is minimised. The activity range of interferent was between 0 and 34.08×10^{-3} mol dm^{-3} and between 0 and 29.40×10^{-1} mol dm^{-3} for IO_4^- and IO_3^- respectively.

The extent of reaction of periodate can be related to the amount of iodide consumed in reaction (1). The iodine

$$IO_4^- + 2I^- + 2H^+ \rightleftharpoons IO_3^- + I_2 + H_2O \qquad (1)$$

produced by the above reaction rapidly [11] combines with iodide producing tri-iodide to further reduce the iodide-ion concentration. An expression relating the amount of periodate consumed in the reaction to the decrease in the iodide concentration was derived [equation (2)] where $[I^-]$

$$[IO_4^-]_0 - [IO_4^-]_t = ([I^-]_0 - [I^-]_t)\Big/\left(2 + \frac{K[I^-]_t}{1 + K[I^-]_t}\right) \qquad (2)$$

and $[IO_4^-]$ are the iodide and periodate concentrations and the subscripts refer to initial concentrations and concentrations at time t. K represents the formation constant for tri-iodide ion. Values of 768, 694, and 629 dm^3 mol^{-1} were used for K at 25.0, 30.0, and 35.0 °C respectively.[12]

RESULTS

Previous studies [3—6] have found that the reaction of periodate with iodide is first order with respect to both species. Integration of expression (3) yields (4). The

$$-d[IO_4^-]/dt = k_1[IO_4^-][I^-] \qquad (3)$$

$$1/([I^-]_0 - 2[IO_4^-]_0)\ \ln\,([IO_4^-]_0[I^-]_t/[I^-]_0[IO_4^-]_t) = k_1 t \qquad (4)$$

iodide concentration at any time, t, was determined by potential measurement. The periodate concentration was calculated by means of the stoicheiometric relationship expressed in equation (2). Evaluation of the left-hand side of equation (4), as shown in Table 1, yielded a linear relationship with respect to time for approximately the first 74% of the reaction. The rate constant, k_1, was determined from this relationship.

The effect of ionic strength, I, at 25.0 °C as evaluated at six specific values of ionic strength, is shown in Table 2.

TABLE 1

Reaction data (25.0 °C, I = 0.02 mol dm^{-3}, pH = 5.31)

Time/s	Δ Potential/ mV	$10^4[I^-]_t$/ mol dm^{-3}	$10^4[IO_4^-]_t$/ mol dm^{-3}	$\left(\frac{1}{[I^-]_0 - 2[IO_4^-]_0}\right) \ln \left(\frac{[IO_4^-]_0[I^-]_t}{[I^-]_0[IO_4^-]_t}\right)$/ dm^3 mol^{-1}
0	0	8.088	1.874	0
11.3	1.4	7.661	1.694	126.72
29.3	2.8	7.254	1.520	271.87
48.8	4.2	6.871	1.355	430.80
71.3	5.6	6.507	1.196	610.56
96.8	7.0	6.162	1.044	817.92
126.8	8.4	5.835	0.898	1 057.54
163.5	9.8	5.526	0.759	1 338.62
207.0	11.2	5.234	0.626	1 677.31
258.0	12.6	4.955	0.497	2 098.94
325.5	14.0	4.692	0.375	2 642.69

Extrapolation to zero ionic strength was made by use of the general relationship [13] shown in equation (5) where k_1^0 is

$$\log k_1 = \log k_1^0 + 2AZ_pZ_qI^{\frac{1}{2}}/(1 + \beta aI^{\frac{1}{2}}) + \sum_{ij} B_{ij}[J] \quad (5)$$

the rate constant at zero ionic strength; Z_p and Z_q are the charges on the reacting species P and Q; A and β are temperature-dependent constants and a is the mean ionic diameter. The constant A has the value 0.511 5, 0.516 1, and 0.521 1 dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ at 25.0, 30.0, and 35.0 °C respectively.[14] As the effective diameter, a, of ions in solution is between 0.3 and 0.5 nm and the constant β [14] is *ca.* 0.33 × 10^{10} dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ m^{-1}, the product βa is approximately unity at the three temperatures studied. B_{ij} is the coefficient for the specific interaction of species I with an oppositely-charged species J, which was Na$^+$ in this set of experiments. From a plot of the term [$\log k_1 - 2AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$] against I (equal to [Na$^+$]) the sum of the specific interaction coefficients, ΣB_{ij}, was determined to be (−0.26 ± 0.04) dm^3 mol^{-1} at 25.0 °C. Thus, the rate constant at zero ionic strength is (5.9 ± 0.1) dm^3 mol^{-1} s^{-1}.

TABLE 2

Effect of ionic strength, I, on the rate constant (25.0 °C, pH = 5.31, $[I^-]_0$ = 8.088 × 10^{-4} mol dm^{-3}, $[IO_4^-]_0$ = 1.874 × 10^{-4} mol dm^{-3})

I/mol dm^{-3}	k_1 */ dm^3 mol^{-1} s^{-1}	$\log k_1 - 2AI^{\frac{1}{2}}$/ $(1 + I^{\frac{1}{2}})$
0.020	7.9 ± 0.3	0.771 ± 0.017
0.030	8.3 ± 0.1	0.768 ± 0.006
0.060	8.8 ± 0.2	0.743 ± 0.010
0.085	9.6 ± 0.2	0.751 ± 0.009
0.110	9.7 ± 0.4	0.732 ± 0.018
0.210	11.0 ± 0.2	0.720 ± 0.008

* Average of three determinations. Standard deviation shown.

The effect of hydrogen-ion concentration was determined in a series of triplicate experiments at 25.0 °C and at an ionic strength of 0.075 mol dm^{-3}. The rate constants for the reaction in solutions having pH 4.23, 3.83, 3.64, and 3.51 are 9.8 ± 0.4, 9.7 ± 0.3, 9.6 ± 0.3, and 9.8 ± 0.1 dm^3 mol^{-1} s^{-1} respectively. Within experimental error, no rate dependence on hydrogen-ion concentration was observed in contrast to earlier reports.[3,5]

The rate constant was determined at three ionic strengths, pH = 5.31, at 30.0 °C and 35.0 °C, in addition to the measurement at 25.0 °C, to determine the effect of temperature on the reaction rate. These results are shown in Table 3. The rate constants at zero ionic strength extrapolated from these data are (8.1 ± 0.2) dm^3 mol^{-1} s^{-1} at 30.0 °C and (10.5 ± 0.4) dm^3 mol^{-1} s^{-1} at 35.0 °C. The sums of the specific interaction coefficients are (−0.31 ± 0.06) dm^3 mol^{-1} at 30.0 °C and (−0.30 ± 0.12) dm^3 mol^{-1} at 35.0 °C. From the rate constants at the three temperatures an activation energy of (44 ± 1) kJ mol^{-1}, a pre-exponential term of (3 ± 2) × 10^8 dm^3 mol^{-1} s^{-1}, an enthalpy of activation of (42 ± 1) kJ mol^{-1}, a free energy of activation of (68.59 ± 0.04) kJ mol^{-1}, and an entropy of activation of −(89 ± 3) J mol^{-1} K^{-1} were obtained.

DISCUSSION

A summary of the reported results for the rate of reaction between periodate and iodide ions is presented in Table 4. A feature of our study is the absence of a hydrogen-ion dependence of the reaction rate. Indelli and co-workers [3] determined the rate of reaction by the addition of successive amounts of sodium thiosulphate to the reaction mixture and measurement of the time required for sufficient iodine to be produced to react with thiosulphate as indicated by the appearance of an excess of iodine. Thiosulphate is known to react with both iodate [15,16] and periodate.[17] The rate expression

TABLE 3

Effect of temperature on the rate constant (pH = 5.31, $[I^-]_0$ = 8.088 × 10^{-4} mol dm^{-3}, $[IO_4^-]_0$ = 1.874 × 10^{-4} mol dm^{-3})

θ_c/°C	I/mol dm^{-3}	k_1 */ dm^3 mol^{-1} s^{-1}	$\log k_1 - 2AI^{\frac{1}{2}}$/ $(1 + I^{\frac{1}{2}})$
30.0	0.020	10.9 ± 0.5	0.909 ± 0.021
30.0	0.060	12.1 ± 0.4	0.878 ± 0.015
30.0	0.210	14.7 ± 0.1	0.844 ± 0.004
35.0	0.020	14.4 ± 0.4	1.029 ± 0.012
35.0	0.060	15.4 ± 0.1	0.982 ± 0.004
35.0	0.210	19.4 ± 0.7	0.961 ± 0.016

* Average of three determinations, except at 30.0 °C, I = 0.210 mol dm^{-3} and at 35.0 °C, I = 0.060 mol dm^{-3}, which are the averages of two determinations. Standard deviation shown.

for the former[18,19] shows it to be slow relative to the reaction of iodine with thiosulphate[20] and to that of iodide and periodate. The effect of adding thiosulphate may not be negligible. A brief investigation of the reaction of periodate with thiosulphate has revealed that this reaction occurs to an appreciable rate and exhibits a pH dependence. The pH dependence reported[3] is thus possibly not that of the periodate reaction with iodide but an artefact.

The ionic-strength dependence of the observed rate constant (see Table 2) are consistent with the charges of the species involved in the rate-limiting step being of the same sign and of unit magnitude since the slope of a log k_1 against $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ plot is 0.75 ignoring the $\sum_{ij} B_{ij}[J]$ term in equation (5). This excludes the possibility of neutral species in the rate-limiting step. Periodate exists in acidic solution in several forms, mainly IO_4^-, H_5IO_6, $H_4IO_6^-$, and $H_3IO_6^{2-}$.[21] From the equilibrium constants for these species at 25 °C,[21] it can be calculated that *ca.* 96% of the total periodate exists as IO_4^- and 2.4% as $H_4IO_6^-$ within the pH range studied. The equilibria are reported to be rapidly established and pH dependent,[22] except for that between IO_4^- and $H_4IO_6^-$, which has been reported[23] to be pH independent.

TABLE 4

Summary of results obtained from studies of the periodate–iodide reaction

k_0/ dm^3 mol^{-1} s^{-1}	Activation energy/ kJ mol^{-1}	Pre-exponential factor/ dm^3 mol^{-1} s^{-1}	pH dependence	Ref.
ca. 6.33			None observed at low [acetate] [a]	4
22.0			2nd order, $k_H = 2.3 \times 10^5$ dm^9 mol^{-3} s^{-1} [b]	5
3.55	50.0	2.1×10^9	Not investigated [a]	6
4.53	42.5	1.8×10^8	1st order, $k_H = 2.89 \times 10^3$ dm^6 mol^{-2} s^{-1} [c]	3
5.9 ± 0.1	44 ± 1	$(3 \pm 2) \times 10^8$	None observed [a]	This work

[a] Acetate buffer medium. [b] Sulphuric acid medium. [c] Perchloric acid medium.

Although most redox and replacement reactions involving oxyanions have a rate law with a hydrogen-ion term, such is not the case with the periodate–iodide reaction. It has been suggested[24] that the role of the protons in oxyanion reactions is to labilise the oxygen by converting it to the hydroxide form. As several of the oxygen atoms of $H_4IO_6^-$ are already protonated and as such labilised, it seems likely that this species is the reactive form of periodate and accounts for the lack of hydrogen-ion dependence in the rate-limiting step.

The authors thank A.E.C.I. for a fellowship (to C. C.) and the South African C.S.I.R. for support of this study. The authors also thank one of the referees for his suggestions in the revision of this paper.

[9/858 *Received, 4th June,* 1979]

REFERENCES

[1] C. Efstathiou and T. P. Hadjiioannou, *Analyt. Chem.*, 1975, **47**, 864.

[2] G. F. Smith, 'Analytical Applications of Periodic Acid and Iodic Acid and their Salts,' 5th edn., G. Frederick Smith Chemical Company, Columbus, Ohio, 1950.

[3] A. Indelli, F. Ferranti, and F. Secco, *J. Phys. Chem.*, 1966, **70**, 631.

[4] E. Abel and A. Furth, *Z. Phys. Chem.*, 1923, **107**, 313.

[5] E. Abel and R. Siebenschein, *Z. Phys. Chem.*, 1927, **130**, 631.

[6] D. Peschanski, *J. Chim. phys.*, 1951, **48**, 489.

[7] J. H. Woodson and H. A. Liebhafsky, *Analyt. Chem.*, 1969, **41**, 1894.

[8] R. A. Hasty, *Mikrochim. Acta*, 1973, 925.

[9] R. Rangarajan and G. A. Rechnitz, *Analyt. Chem.*, 1975, **47**, 324.

[10] K. Srinivasan and G. A. Rechnitz, *Analyt. Chem.*, 1969, **41**, 1203.

[11] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, 1962, **84**, 1355.

[12] M. Davies and E. Gwynne, *J. Amer. Chem. Soc.*, 1952, **74**, 2748.

[13] A. D. Pethybridge and J. E. Prue, 'Inorganic Reaction Mechanisms,' Part 2, ed. J. O. Edwards, Interscience, New York, 1972, vol. 17 in the series 'Progress in Inorganic Chemistry,' ed. S. Lippard, p. 336.

[14] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworth Scientific Publications, 1959, p. 468.

[15] E. Carriere and Juillard, *Compt. rend.*, 1930, **191**, 1133.

[16] E. Carriere and L. Fayssr, *Compt. rend.*, 1935, **201**, 1036.

[17] E. Carriere and M. Delpla, *Compt. rend.*, 1937, **205**, 1157.

[18] R. Rieder, *J. Phys. Chem.*, 1930, **34**, 2111.

[19] A. Indelli, *J. Phys. Chem.*, 1961, **65**, 240.

[20] A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1341.

[21] C. Crouthamel, A. Hayes, and D. Martin, *J. Amer. Chem. Soc.*, 1951, **73**, 82.

[22] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1972, p. 480.

[23] K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, 1964, **68**, 3869.

[24] E. Chaffee and J. O. Edwards, 'Inorganic Reaction Mechanisms,' Part 1, ed. J. O. Edwards, Interscience, New York, 1970, vol. 13 in the series 'Progress in Inorganic Chemistry,' ed. S. Lippard, p. 205.