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Authors

Chia, Yuan-tsan
Connick, Robert E.

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THE RATE OF OXIDATION OF I^- TO HYPOIODITE
ION BY HYPOCHLORITE ION

Yuan-tsan Chia and Robert E. Connick

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The Rate of Oxidation of I^- to Hypiodite
Ion by Hypochlorite Ion

Yuan-tsan Chia and Robert E. Connick

In studying the behavior of iodine in the +1 oxidation state in alkaline solution,⁽¹⁾ it was convenient to prepare IO^- solutions by

(1) Y.-t. Chia, Thesis, University of California, Berkeley, June, 1958;
University of California Radiation Laboratory Report UCRL-8311, June 2, 1958.

the oxidation of iodide ion by hypochlorite ion. Under most of our conditions this reaction appeared to be instantaneous as judged by spectrophotometric observations, however at high hydroxide and low iodide concentrations at least part of the change from the hypochlorite spectrum to the hypiodite spectrum occurred at a detectable rate. A fast mixing technique was then applied to make the reaction more readily measurable.

The net reaction was shown to be

by studying the stoichiometry spectrophotometrically at varying ratios of I^- to ClO^- .⁽¹⁾ For interpreting the rate data the rate constant k' was defined:

$$+ \frac{d(IO^-)}{dt} = k'(I^-)(ClO^-) \quad (2)$$

where parentheses indicate concentrations in moles per liter. In Table 1 are given values of k' at a variety of experimental conditions. It is

seen that the rate is first order in (I^-) and (ClO^-) , a result also borne out by the time dependence of the individual runs. In the last column is the rate constant k which incorporates an inverse hydroxide dependence:

$$\frac{d(IO^-)}{dt} = \frac{k(I^-)(ClO^-)}{(OH^-)} \quad (3)$$

Table 1

Rate Data for Oxidation of I^- by IO^- Temp. $25^\circ C$, Ionic Strength 1.00M

Initial Concentrations				$k', M^{-1} \text{ sec}^{-1}$	$k, \text{ sec}^{-1}$
$(ClO^-) \times 10^3, M$	$(I^-) \times 10^3, M$	$(OH^-), M$	$(Cl^-), M$		
4.00	2.00	1.00	0.004	60.3 ± 5	60.3 ± 5
2.00	4.00	1.00	0.002	62.7 ± 5	62.7 ± 5
2.00	2.00	1.00	0.002	60.6 ± 5	60.6 ± 5
2.00	2.00	0.500	0.502	116 ± 10	58.0 ± 5
2.00	2.00	0.250	0.752	234 ± 20	58.5 ± 5

The hypiodite formed is itself unstable with respect to disproportionation to iodate and iodide. Under the conditions chosen for the present study this latter reaction was much slower than the oxidation of iodide by hypochlorite and could be neglected in interpreting the data.

Discussion. Anbar and Taube⁽²⁾ have presented two possible

(2) M. Anbar and H. Taube, J. Am. Chem. Soc. 80, 1073 (1958).

mechanisms for the reaction of halide ions with hypohalite ions:

$X^- + YO^- = XO^- + Y^-$, when the form of the rate law is that found in the present study (Equation 2). In the first mechanism the halide ion attacks the oxygen of the hypohalous acid. For our case the steps would be

In the second mechanism the halide ion attacks the halogen of the hypohalous acid to yield the halogen molecule, which subsequently hydrolyzes to yield HOX and Y^- :

Using the unpublished experimental results of Anbar and Rein they concluded that the exchange of bromine between Br^- and HOBr proceeds by attack of the Br^- on the oxygen of HOBr , corresponding to the first mechanism. No conclusion could be drawn about the exchange of chlorine between Cl^- and HOCl . From a comparison of several rate constants they reached the tentative conclusion that the reaction between Br^- and ClO^- , with rate law analogous to Equation (3),⁽³⁾ goes by the first mechanism

(3) L. Farkas, M. Lewin and R. Block, J. Am. Chem. Soc. 71, 1988 (1949).

also. From the above results no definite extrapolation can be made to the $\text{I}^- - \text{ClO}^-$ reaction, although the first mechanism would seem more likely.

Experimental

The reaction was followed spectrophotometrically on a Cary recording spectrophotometer. The rapid mixing was accomplished by injection with a hypodermic syringe, following the method developed by Stern and DuBois⁽⁴⁾

(4) K. G. Stern and D. DuBois, J. Biol. Chem. 116, 575 (1936).

and later applied by Below.⁽⁵⁾ The 2.15 cm absorption cell was that used

(5) J. F. Below, Jr., University of California Radiation Laboratory Report UCRL-3011, June, 1955.

by Below. Eight ml of solution with the desired hydroxide and hypochlorite concentrations were placed in the cell and the absorption recorded on the chart. Iodide solution containing the same hydroxide concentration as that in the cell was introduced into a hypodermic syringe through a No. 16 needle. The syringe was filled to the 2 ml mark with care being taken to avoid bubbles. With the Cary spectrophotometer recording at 400.6 mμ, the syringe was quickly emptied manually with the tip of the needle just below the surface. The measurement of absorbance was carried on as a function of time at the fixed wave length.

Zero time was taken as the point at which the absorbance on the spectrophotometer chart began to rise. Other times were calculated

from the running speed of the chart. A typical set of points (third experiment of Table I) read from the chart is shown in Fig. 1 where the absorbance is plotted against time in seconds. Slopes read from such plots yielded values of $d(IO^-)/dt$ for calculation of k' by Equation (2). The molar absorptivity of IO^- and ClO^- at 400.6 $m\mu$ are 38.5 and 0.510 respectively.⁽¹⁾ Since the exact time of mixing (~ 1 sec) was not known, the zero time was somewhat uncertain. The use of derivatives eliminated the need for zero time in the treatment of the data.

The syringe was carefully lubricated with a small amount of Kel-F No. 90 grease in the part above the 2.5-ml mark. Too thin a layer gave rise to bubble formation. A qualitative test showed that the attack of the stainless steel needle by hypochlorite was unimportant. No effect was found on reversing the order of mixing by injecting hypochlorite into iodide.

In the hydroxide dependence experiments the ionic strength was held constant by the addition of sodium chloride.

Fig. 1.