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Kinetics and Mechanism of the Oxidation of Iodine by Chlorite Ion[1]

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The stoichiometry of the reaction between chlorite and iodine in the pH range 2–5 and at low $[I^-]$ has been determined to be $5ClO_2^- + 2I_2 + 2H_2O \rightarrow 5Cl^- + 4IO_3^- + 4H^+$. The kinetics of this reaction have been studied by stopped-flow spectrophotometry at 22.2 °C and variable ionic strength (10^{-2}–10^{-1} M). The rate law is $-{}^1/_2 d[I_2]/dt = (k_1[ClO_2^-] + k_2[ClO_2^-]/[H^+] + k_3)[I_2]$, where $k_1 = (1.1 \pm 0.4) \times 10\ M^{-1}\ s^{-1}$, $k_2 = (1.1 \pm 0.1) \times 10^{-2}\ s^{-1}$, and $k_3 = (5.4 \pm 0.3) \times 10^{-1}\ s^{-1}$. A mechanism is proposed involving formation of the key intermediate $IClO_2$ by reactions between chlorite and I_2, I_2OH^-, and IOH_2^+. The rate constant for the elementary reaction $ClO_2^- + I_2 \rightarrow IClO_2 + I^-$ is given by k_1. The value of the rate constant for the elementary reaction $I_2OH^- + ClO_2^- \rightarrow IClO_2 + I^- + OH^-$ is $7.7 \times 10^7\ M^{-1}\ s^{-1}$. We have identified k_3 with the reaction $I_2 + H_2O \rightarrow IOH_2^+ + I^-$.

Introduction

Recently, a family of homogeneous chemical oscillators has been designed on the basis of reactions between chlorite and iodide, iodine, and oxyiodine species.[2] Reaction between chlorite and iodide is complex, showing "clock" behavior in batch and bistability and oscillations in a flow reactor.[3] If enough iodide is added to chlorite so that some I^- remains unreacted, a Landolt-type[4] clock reaction results: after a predictable delay, a deep brown color rapidly appears. If it is the chlorite that remains unreacted, a ferrous–nitric acid[5] type of clock reaction results: stages of delay, deep color, and abrupt fading of color follow each other successively. The delay and deep color formation are due to the autocatalytic buildup of iodine and triiodide ion; the abrupt disappearance of color results from the reaction between chlorite and the above iodine species.

The reaction between chlorite and iodide to produce iodine was studied by Bray,[6] who determined the stoichiometry to be

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + 2H_2O + Cl^- \qquad (I)$$

The kinetics and mechanism of this reaction were later investigated by two different groups[7,8] using "classical" kinetics methods. Both sets of investigators concluded that the abrupt disappearance of the brown color in the case of excess ClO_2^- was due to further oxidation of iodine by chlorite. The composite "clock" reaction is then

$$3ClO_2^- + 2I^- \rightarrow 2IO_3^- + 3Cl^- \qquad (II)$$

The rapidity of the "shut-off" reaction precluded a kinetics study by either of the two groups that investigated the overall reaction.

In this paper we report such a study by rapid-mixing spectrophotometry. We show that the stoichiometry of the reaction between chlorite and iodine in the absence of initially added iodide is

$$5ClO_2^- + 2I_2 + 2H_2O \rightarrow 5Cl^- + 4IO_3^- + 4H^+ \qquad (III)$$

which had been proposed by Bray.[6]

Experimental Section

Reagent grade chemicals were used without further purification. Solutions were prepared with doubly distilled water. Sodium chlorite stock solutions contained 0.001 M sodium acetate to maintain an alkaline pH, which retards decomposition and also constitutes part of the buffering system after mixing (except as noted below). Iodide, a contaminant of even the purest iodine reagents, was minimized by addition of potassium iodate to the iodine stock solutions. The iodate scavenges iodide by the Dushman reaction: [4b] $5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O$. The concentrations of iodine stock solutions were determined by volumetric titration with standardized sodium thiosulfate solutions.

Experiments were carried out with reaction mixtures buffered at pHs ranging from 2.69 to 4.39. Glacial acetic acid was pipetted into the iodine solutions in concentrations depending upon the pH desired in the reaction vessel. When this solution was mixed with the acetate-containing chlorite solution, the appropriate buffer was generated in situ. For the lowest pH, an acetic acid–acetate buffer was inappropriate, and a premixed buffer (0.0263 M H_2SO_4, 0.1 M Na_2SO_4) was used. Measurements of pH were made after mixing on an Orion Research Digital Ionalyzer, Model 801A. Ionic strength varied in these experiments from approximately 10^{-2} to 10^{-1} M, due mainly to sodium chlorite, acetate, or sulfate.

The apparatus was a Gibson-type stopped-flow spectrophotometer,[9] with thermostating of both reservoirs and of the pushing syringes to 22.2 ± 0.2 °C. Each change in absorbance at 460 nm with time was captured on a storage oscilloscope and photographed. The analytical concentration of I_2 in reacting mixtures was calculated from the transmittance data at 460 nm. Other wavelengths where absorbance changes could be detected gave similar results.

Results

Stoichiometry. While Bray's proposed stoichiometry,[6] eq III, is chemically reasonable and thermodynamically favorable ($\Delta G° \approx -25$ kcal mol^{-1} at 25 °C), he did not verify it experimentally. Since other products, for example, HOCl, in place of Cl^-, are also thermodynamically possible, and since the kinetics analysis rests to some extent on having the correct stoichiometry, we first undertook to establish the stoichiometry of the reaction.

In one experiment, an excess of iodine (31.4 mmol I_2) was added to a sodium chlorite solution (2.18 mmol) to make a

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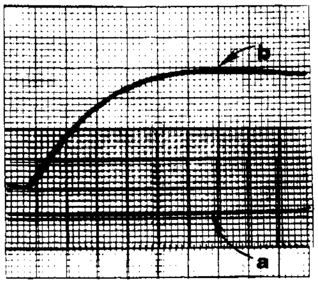

Figure 1. Stopped-flow control experiments. Trace a is a (reversed) oscillograph of an experiment in which a buffered iodine solution containing iodate is mixed with buffer. No reaction is detected. Experimental data: $[I_2] = 2.74 \times 10^{-4}$ M, $[IO_3^-] = 9.3 \times 10^{-5}$ M, pH 3.0, acetic acid–acetate buffer. Trace b is with the same solutions mixed as in a but with *no* iodate added to the iodine solution. Note the delay time before the trace begins to rise. The vertical axis is proportional to increasing transmittance at 460 nm. The horizontal axis is increasing time, 0.5 s/major division.

final volume of 100 mL. Unreacted I_2 was removed by extraction with CCl_4 and determined by titration with sodium thiosulfate. The iodate product was treated with acidified 0.01 M KI to form iodine, which was likewise determined by thiosulfate titration. In this experiment, the ratio of millimoles of iodine reacted to millimoles of chlorite initially present was $0.916/2.18 = 0.42 \approx 2/5$.

Experiments were carried out with excess chlorite; for example, 100 mmol of chlorite was reacted with 15.7 mmol of iodine. The unreacted chlorite was removed by acidification and boiling for 1 h. The iodate produced in the reaction was determined by adding KI and titrating the liberated iodine with thiosulfate. In this experiment, the ratio of millimoles of iodate produced to millimoles of iodine initially present was $31.5/15.7 = 2.01$.

Kinetics. A. Control Experiments. Since chlorous acid and other components or combinations of components of these reaction mixtures are unstable, it is important to identify and eliminate artifactual effects. Therefore, control experiments, especially those in which single reagents were mixed with buffer, were carried out.

All reactions were monitored at 460 nm, where I_2 absorbs (absorptivity coefficient = $\epsilon^{460}_{I_2}$ 770 cm^{-1} M^{-1}).[10a] Another iodine species absorbing appreciably at this wavelength is I_3^- ($\epsilon^{460}_{I_3^-}$ 1030 cm^{-1} M^{-1}).[10b] The triiodide contribution is negligible at low iodide concentrations and will be ignored.[10b]

When a saturated iodine solution acidified with glacial acetic acid, approximately 100 μM in KIO_3, is mixed with a solution 10^{-3} M in sodium acetate, no discernible reaction is observed (Figure 1, trace a). A repeat of the experiment without adding KIO_3 results in the reaction response shown in Figure 1, trace b. Effects such as trace b (Figure 1), observed in control experiments in the absence of added iodate, were present even when iodine was reacted with chlorite in the absence of added iodate. Trace b (Figure 1) shows a delay, followed by a reaction. The time constants of reaction effects such as the one shown in Figure 1, trace b, were independent of chlorite concentration but depended on pH. Deliberate addition of iodide to such reaction mixtures extended the delay time but did not affect the time constant of the reaction response.

We assign the reaction effect shown in Figure 1, trace b, to reactions involving only iodine-containing species. This effect may be due entirely, or partly, to steps in the Dushman reaction.[4b] In any case, this spurious effect can be avoided by adding iodate to the reacting iodine solutions. This precaution has prevented us from varying iodide concentrations in the rate-law determination.

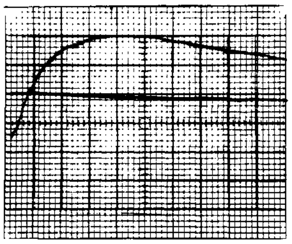

Figure 2. Oscillograph of stopped-flow experiment showing formation of chlorine dioxide. Initial disappearance of iodine over the first 5 s is followed by a decrease in light transmittance due to ClO_2 buildup. The oscilloscope was triggered a second time to show continuing slow reaction. Experimental data: $[I_2] = 2.74 \times 10^{-4}$ M, $[ClO_2^-] = 1.2 \times 10^{-2}$ M, $[IO_3^-] = 9.3 \times 10^{-5}$ M, pH 3.18. The vertical axis is proportional to increasing light transmittance at 460 nm. The horizontal axis is increasing time, 1 s/major division.

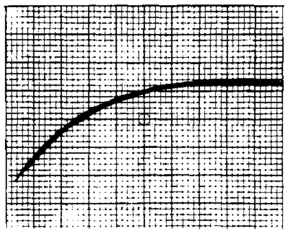

Figure 3. Oscillograph of stopped-flow experiment assigned to oxidation of iodine by chlorite. Experimental data: $[I_2] = 3.42 \times 10^{-4}$ M, $[ClO_2^-] = 1.5 \times 10^{-2}$ M, $[IO_3^-] \approx 10^{-4}$ M, pH 3.31. Oscillograph: vertical axis 50 mV/major division, 0–100% transmittance = 500 mV; horizontal axis 100 ms/major division.

Table I. Pseudo-First-Order Rate Constant k as a Function of $[I_2]$ ($[ClO_2^-] = 1.2 \times 10^{-2}$ M)

$10^4[I_2]$, M	pH	k, s^{-1} (no. of trials)
8.22	3.05	0.65 ± 0.05 (4)
3.42	3.09	0.66 ± 0.04 (3)
1.37	3.05	0.62 ± 0.02 (4)
1.03	2.98	0.65 ± 0.05 (4)

Mixing chlorite–acetate solutions against glacial acetic acid produced no detectable effect in the time range (<1 s) of the kinetics studies reported here. However, ClO_2 absorbs at the wavelength used to monitor I_2 disappearance ($\epsilon^{460}_{ClO_2}$ 32 cm^{-1} M^{-1}).[11] With an acid dissociation constant $K_a = [H^+] \cdot [ClO_2^-]/[HClO_2] = 10^{-2}$ M,[12] chlorous acid is produced from chlorite at low pH. Chlorous acid is unstable, decomposing by a complex process to give ClO_2 at a rate that increases with increasing $[H^+]$.[12] The production of ClO_2 in solutions containing excess chlorite may account for the increase in absorbance at 460 nm after a reaction has apparently gone to completion (Figure 2). This effect was only observed at low pHs and at times >5 s, i.e., at times longer than required for reaction III.

The appearance of this effect set a lower limit to the pH range under investigation.[13] An upper limit of pH 5 was required to avoid products other than iodate and chloride. Within this pH range, in the presence of previously added iodate, we observe a spectrometric response (Figure 3) in mixtures of iodine and chlorite, which we have assigned to reaction III.

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(10) (a) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842–1843. (b) Allen, T. L.; Keefer, R. M. *Ibid.* **1955**, *77*, 2957–2960.

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(13) Since all of our studies were done at pHs considerably above the pK_a of $HClO_2$, this species was not present in significant concentration in any of our experiments, and the present work gives no relevant information about the reaction between chlorous acid and I_2.

Table II. Observed and Calculated Pseudo-First-Order Rate Constants ($[I_2] = 3.42 \times 10^{-4}$ M)

$[ClO_2^-]$, M	pH	no. of trials	k, s^{-1} obsd	k, s^{-1} calcd[a]
5.0×10^{-3}	3.17	5	0.63 ± 0.04	0.68
7.5×10^{-3}	3.17	4	0.74 ± 0.01	0.74
1.0×10^{-2}	3.17	5	0.97 ± 0.13	0.81
1.25×10^{-2}	3.17	4	1.2 ± 0.1	0.88
1.5×10^{-2}	3.17	4	1.2 ± 0.1	0.95
2.0×10^{-2}	3.17	4	1.2 ± 0.1	1.1
2.5×10^{-2}	3.17	4	1.5 ± 0.1	1.2
3.5×10^{-2}	3.17	4	1.6 ± 0.1	1.5
4.05×10^{-2}	3.17	4	1.7 ± 0.1	1.6
4.5×10^{-2}	3.17	4	1.9 ± 0.1	1.8
1.0×10^{-1}	3.17	4	3.4 ± 0.4	3.3
3.0×10^{-2}	4.61	4	8.4 ± 0.2	8.9
3.0×10^{-2}	3.97	5	3.9 ± 0.3	3.9
3.0×10^{-2}	3.47	5	3.1 ± 0.3	1.8
3.0×10^{-2}	3.39	3	2.4 ± 0.5	1.7
3.0×10^{-2}	3.31	5	1.8 ± 0.3	1.5
3.0×10^{-2}	3.23	4	1.2 ± 0.1	1.4
3.0×10^{-2}	3.12	5	1.2 ± 0.1	1.3
3.0×10^{-2}	2.84	4	1.1 ± 0.1	1.1
3.0×10^{-2}	2.69	4	0.65 ± 0.05	1.0
1.5×10^{-5}	3.15	4	0.46 ± 0.20	0.54
1.5×10^{-4}	3.15	4	0.59 ± 0.11	0.54
5.0×10^{-5}	3.00	4	0.51 ± 0.17	0.54

[a] Calculated from eq 1 with the rate constants given in the text.

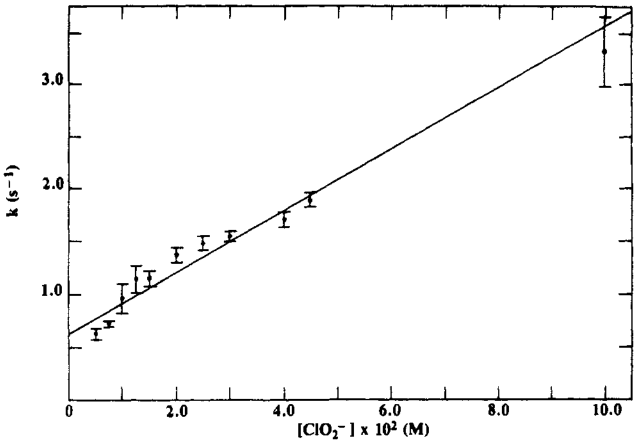

Figure 4. Chlorite dependence. Experimental data: $[I_2] = 3.42 \times 10^{-4}$ M, pH 3.17, $[IO_3^-] \approx 10^{-4}$ M. Error bars represent standard deviations from the experimental mean. The solid line is the best fit of form $a + b[ClO_2^-]$ with $a = 1.0\ s^{-1}$ and $b = 6.3 \times 10\ M^{-1}\ s^{-1}$.

B. Rate Studies. The order of the reaction with respect to I_2 was determined in the presence of excess chlorite (15- to 116-fold excess). Semilog plots of transmittance vs. time were linear at all concentrations studied, implying a first-order dependence on $[I_2]$. Values of k, the pseudo-first-order rate constant, were obtained by using a least-squares fit to the function ln $(T_t - T_\infty)$ plotted against time, where T_t is the transmittance at time t, and T_∞ is the transmittance after no further reaction is observed. In Table I, we show that the values obtained for k are, as expected, independent of $[I_2]$ at fixed $[ClO_2^-]$ and pH.

For the determination of the order with respect to chlorite, the pseudo-first-order rate constant, k, at constant $[I_2]$ was plotted against the concentration of excess chlorite. The results are collected in Table II and are shown graphically in Figure 4. The linearity of the plot, with a finite intercept, indicates that two processes are present: one first order in $[ClO_2^-]$, the other zero order in $[ClO_2^-]$.

The variation in pseudo-first-order rate constant with $[H^+]$ is shown in Table II and Figure 5. The rate of the reaction is observed to increase with decreasing $[H^+]$. The plot of rate constant vs. $[H^+]$ levels off at a value equal, within experimental error, to the intercept in Figure 4 and corresponds to the zero-order term. An $[H^+]$ dependence of this term was undetectable in these experiments.

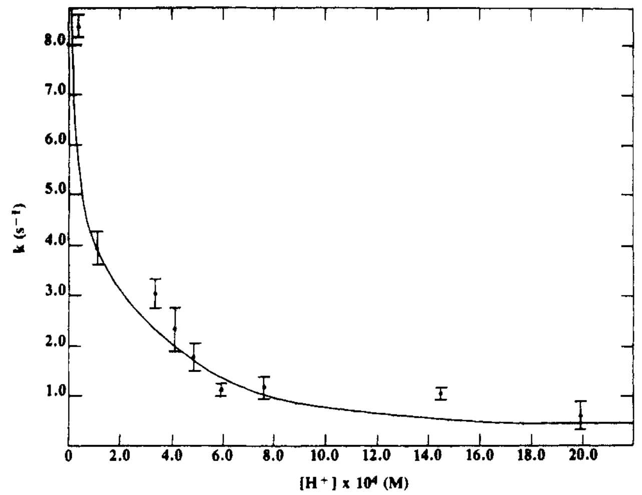

Figure 5. Hydrogen ion dependence. Experimental data: $[I_2] = 3.42 \times 10^{-4}$ M, $[ClO_2^-] = 3.0 \times 10^{-2}$ M, $[IO_3^-] \approx 10^{-4}$ M. Error bars represent standard deviations from the experimental mean. The solid line is the best fit of form $A + B/[H^+]$ with $A = 1.5\ s^{-1}$ and $B = 6.2 \times 10^{-4}\ M^{-1}\ s^{-1}$.

Analysis of these data shows that at a fixed chlorite concentration, k varies as $A + B/[H^+]$. Combining this result with the rate dependences on $[ClO_2^-]$ and $[I_2]$, we obtain a rate law for reaction III of the form

$$-\frac{1}{2}\frac{d[I_2]}{dt} = \left(k_1[ClO_2^-] + k_2\frac{[ClO_2^-]}{[H^+]} + k_3\right)[I_2] \quad (1)$$

A least-squares fit of all 23 data points contained in Table II yields the following values of the rate constants in eq 1, where the error bounds are estimated by comparing the results of the full three-parameter fit with the two-parameter fits obtained by fitting the single-species variation data:

$$k_1 = (1.1 \pm 0.4) \times 10\ M^{-1}\ s^{-1}$$

$$k_2 = (1.1 \pm 0.1) \times 10^{-2}\ s^{-1}$$

$$k_3 = (5.4 \pm 0.3) \times 10^{-1}\ s^{-1}$$

Mechanism

An important reaction to consider in devising a mechanism is the hydrolysis of iodine, $I_2 + H_2O = HOI + H^+ + I^-$. For the following reasons, we believe that this reaction is not rate determining in the reaction between chlorite and iodine. (1) Its rate constants have been measured.[14] The forward rate constant, 3.0 s^{-1} at 20 °C, is larger than k_3. (2) If the hydrolysis were important, adding iodate should increase [HOI], and hence the rate of the reaction, by removing I^-. In fact, varying the iodate concentration from 2.00×10^{-2} to 4.67×10^{-7} M at constant pH does not have a detectable effect on the value of k. (3) As shown below, the reaction of HOI with I^- to regenerate I_2 is faster than its reaction with ClO_2^-.

Chlorite and iodate could react to produce chlorine dioxide and IO_2. This reaction should be unimportant in our system, as we have observed it to be too slow to compete with the iodine reaction. The analogous reaction between chlorite and chlorate has been reported by Taube and Dodgen to be very slow in acid.[15]

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(14) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355–1361.
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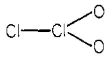
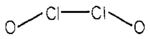
In the same wide-ranging study on the mechanisms of reactions involving changes in the oxidation state of chlorine, Taube and Dodgen have shown that several of these reactions proceed via a common intermediate of composition Cl_2O_2 and structure



or Cl–O–Cl–O but *not*



In analogy to this postulate, we assume, as rate-determining steps for the processes described by rate constants k_1 and k_2, the formation of an intermediate of composition $IClO_2$. The process associated with k_3 is postulated to involve the rate-determining formation of a precursor, IOH_2^+, of the same intermediate $IClO_2$.

We then find three processes—A, B, and C—with associated rates v_A, v_B, and v_C for formation of $IClO_2$. Process A is

$$ClO_2^- + I_2 \xrightarrow{k_1} IClO_2 + I^- \tag{A1}$$

$$v_A = k_1[ClO_2^-][I_2] \tag{2}$$

where we have identified k_1 with the elementary reaction between ClO_2^- and I_2, $k_1 = 11\ M^{-1}\ s^{-1}$.

Process B is a reaction between I_2OH^- and ClO_2^-. We

$$H_2O = H^+ + OH^- \quad \text{fast equilibrium, } K_w \tag{B1}$$

$$I_2 + OH^- = I_2OH^- \quad \text{fast equilibrium, } K_b \tag{B2}$$

$$I_2OH^- + ClO_2^- \xrightarrow{k_2'} IClO_2 + I^- + OH^- \tag{B3}$$

$$v_B = k_2'K_bK_w[ClO_2^-][I_2]/[H^+] \tag{3}$$

identify k_2 with the elementary steps in process B and calculate, from $k_2 = 1.1 \times 10^{-2}\ s^{-1}$, $K_w = 10^{-14}\ M^2$, and $K_b = 1.3 \times 10^4\ M^{-1}$,[14] that $k_2' = 7.7 \times 10^7\ M^{-1}\ s^{-1}$. This last value is about 1 order of magnitude less than the expected value of a diffusion-controlled reaction between species of this charge type.[16]

Process C contains a rate-determining step in which only iodine is involved. Since the hydrolysis of I_2 to yield HOI has a rate constant 6 times greater than k_3, we consider the alternative hydrolysis pathway, i.e., formation of hydrated I^+. Then

$$I_2 + H_2O \underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}} IOH_2^+ + I^- \tag{C1}$$

is followed by

$$IOH_2^+ + ClO_2^- \xrightarrow{k_f} IClO_2 + H_2O \tag{C2}$$

The steady-state approximation on IOH_2^+ in (C1) and (C2) yields

$$v_3 = \left(\frac{k_fk_3'[ClO_2^-]}{k_{-3}'[I^-] + k_f[ClO_2^-]}\right)[I_2] \tag{4}$$

In our experiments, $[ClO_2^-]$ is typically $\sim 10^{-2}$ M and we estimate that $[I^-] < 10^{-7}$ M due to the presence of iodate. The reactions characterized by k_{-3}' and k_f both involve transfer of I^+ from IOH_2^+ to an anion. We expect these rate constants to be similar and close to the diffusion-controlled limit. In that case, we have $k_{-3}'[I^-] << k_f[ClO_2^-]$ and eq 4 reduces to

$$v_3 = k_3'[I_2] \tag{5}$$

so that k_3' may be identified with k_3.

Bell and Gelles[17] have measured the equilibrium constant $K_3' = k_3'/k_{-3}'$ at 25 °C and obtain a value of 1.2×10^{-11} M at zero ionic strength. Combined with our value of k_3, this gives $k_{-3}' = 4.5 \times 10^{10}\ M^{-1}\ s^{-1}$, which is about right for a diffusion-controlled reaction between two singly charged ions of opposite sign.[16]

Since the hydrolysis of I_2 to yield HOI is faster than reaction C1, we must consider why a pathway that is parallel to (C1) and (C2) but involves HOI in place of IOH_2^+ does not contribute to the observed rate law. Analysis of that pathway gives an expression for v_3 similar to that in eq 4 but with k_f, k_3', and k_{-3}' replaced by the corresponding rate constants for the HOI pathway. In order for that expression to be negligible compared with v_3 in eq 4, we must have

$$\bar{k}_{-3}'[H^+][I^-] >> \bar{k}_f[ClO_2^-] \tag{6}$$

where the barred rate constants refer to HOI reactions. Eigen and Kustin[14] determined $\bar{k}_{-3}'$ to be $3.1 \times 10^{12}\ M^{-2}\ s^{-1}$. At a typical pH of 3, we obtain an upper limit on $\bar{k}_f$, the rate constant for the reaction $HOI + ClO_2^- \rightarrow IClO_2 + OH^-$: $\bar{k}_f < 3 \times 10^4\ M^{-1}\ s^{-1}$.

Formation of IO_3^- from $IClO_2$ requires further reactions. In complicated systems such as this one, many sequences of rapid reactions may be imagined, most of which are plausible. One such sequence is given by a eq R1–9.

$$IClO_2 + H_2O = HIO_2 + HOCl \tag{R1}$$

$$HOCl + I^- = HOI + Cl^- \tag{R2}$$

$$ClO_2^- + HOI + H^+ = HIO_2 + HOCl \tag{R3}$$

$$ClO_2^- + HIO_2 = IO_3^- + HOCl \tag{R4}$$

$$IClO_2 + H_2O = IO_3^- + Cl^- + 2H^+ \tag{R5}$$

$$HOCl + HIO_2 = IO_3^- + Cl^- + 2H^+ \tag{R6}$$

$$HOCl + HOI = HIO_2 + Cl^- + H^+ \tag{R7}$$

$$H^+ + I^- + HOI = I_2 + H_2O \tag{R8}$$

$$HIO_2 + I^- + H^+ = 2HOI \tag{R9}$$

Discussion

Formation of IO_3^- from I_2 according to reaction III requires transfer of oxygen to iodine. It is therefore reasonable that I_2OH^- be more reactive than I_2. First, I_2OH^- is polar, whereas I_2 is not. Thus, there is a site for nucleophilic attack on I_2OH^- (presumably the central iodine) by the negatively charged oxygen of chlorite. Second, the OH^- group should weaken the I–I bond, making I^- a better leaving group in process B than in process A.

In his study of the chlorite–iodine reaction, Bray noted that addition of iodide to the reaction mixture caused a delay.[6] We have observed the same effect, although on a shorter time scale, and note, as did Bray, that an unambiguous determination of the kinetics of this reaction should be carried out in solutions of low $[I^-]$. This effect might arise from the Dushman reaction and/or from a shift in the positions of the equilibria in reactions A1, B3, and C1.

It is possible that ICl exists in these solutions[18] and that its hydrolysis is rate determining in one of our processes, e.g., C. Analysis of such a pathway shows that k_3 would then depend

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(16) Jordan, P. C. "Chemical Kinetics and Transport"; Plenum Press: New York, 1979.

(17) Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734–2740. For a review of evidence bearing on the existence of H_2OI^+, cf.: Arotsky, J.; Symons, M. C. R. *Q. Rev., Chem. Soc.* **1962**, *16*, 282–297. Note that this species is not protonated HOI but rather more akin to a hydrated I^+.

(18) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1964; pp 63–65.

upon the ratio $[\mathrm{Cl^-}]/[\mathrm{I^-}]$. As $[\mathrm{Cl^-}]$ increases during the course of the reaction and no variation (within experimental error) of k_3 was observed, we conclude that this pathway is unimportant in these studies.

The chlorite–iodide clock reaction, run under conditions of excess chlorite, has a "spectacularly abrupt fadeout", due to the disappearance of iodine.[7] The reaction responsible for this effect is chlorite–iodine, which had previously been reported to be "quasi instantê".[8] We have shown that this reaction requires about 100 to 800 ms, depending on pH and concentrations. This work, together with the previous studies of the chlorite–iodide reaction[7,8] and an analysis of this reaction in a continuous-flow stirred-tank reactor,[3] should make it possible (at least in the upper pH range where $HClO_2$ is unimportant)[13] to develop a molecular mechanism for the rich variety of phenomena observed in the chlorite–iodide system.

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Comparison of the Coordination Chemistry and Inductive Transfer through the Metal–Metal Bond in Adducts of Dirhodium and Dimolybdenum Carboxylates

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By the study of the thermodynamics of base binding in systems containing metal–metal bonds, significant observations pertaining to the synergistic interaction between the metals can be made that help in understanding the influence that one metal can have upon the chemistry of a second metal. The effectiveness of the metal π^* to ligand π^* back-bonding interaction, which was found to play such an important role in the chemistry of the 1:1 and 2:1 adducts of dirhodium butyrate, is probed as a function of both the ancillary ligand (butyrate vs. perfluorobutyrate) and the metal atom (Rh(II) vs. Mo(II)). Study of the $\mathrm{Mo^{IV}}_2$ system provides strong support for our earlier interpretation of the thermodynamic data for the $\mathrm{Rh^{IV}}_2$ system in terms of π-back-bond stabilization. The change in the base-binding characteristics of the second metal center that accompanies coordination of a base to the primary metal site was also studied as a function of these variables. Results indicate that increasing the electronegativity of the carboxylate group decreases the relative importance of π-back-bonding in the dirhodium system, although such a change has little influence on the inductive transfer to the second metal resulting from coordination of base to the first metal. In addition, it has been shown that the inductive transfer of electrostatic properties of the base is more effective through the shorter Mo–Mo bond than through the longer Rh–Rh bond. On the other hand, the inductive transfer of the base's covalent properties to the second metal center is more effective through the more polarizable Rh–Rh bond than through the quadruple Mo–Mo bond.

Introduction

The understanding and systematic development of a unique reaction chemistry for metal cluster systems require a knowledge of the factors that influence the transmission of electronic effects through metal–metal bonds. Electronic readjustments in the metal–metal bonds of a cluster occur upon coordination of a ligand to one of the metals. These effects not only provide a polarizability mechanism for enhanced ligand binding to the coordinated metal but also influence the subsequent coordination and redox chemistry that occurs at the other interacting metal centers in the cluster. Variations that can be made in the cluster size, the cluster geometry, the metal atoms involved, the electronic nature of the metal–metal bond, and the ancillary ligands provide the potential for a rich and selective chemistry if concepts for the intelligent manipulation of these variables can be developed.

Earlier work from this laboratory[1,2] has focused upon the coordination and redox chemistry of metal-bonded rhodium(II)–rhodium(II) bimetallomers. It was shown[1] that the filled, essentially metal π^* orbitals were very effective at π-back-donation into π-acceptor ligands. This was attributed to a strong interaction between the d_{xz} (and d_{yz}) orbital of one metal with that of a second metal when a direct metal–metal bond exists. The mechanism whereby and extent to which coordination of a base, B, to one metal center influences the acidity of the second metal center could be quantitatively predicted for σ donors with the equation

$$-\Delta H_{2:1} = -\Delta H_{1:1} - kE_B^2 - k'C_B^2 \qquad (1)$$

where E_B and C_B are base parameters from the E and C correlation and k and k' are constant parameters of the cluster that describe the susceptibility of the metal–metal bond to electrostatic and covalent effects.[2] The influence of π back-bonding and σ donation at one center on the ability of the second metal center to undergo these interactions was also determined. The studies demonstrate the utility of thermodynamic studies of base bonding in providing answers to some fundamental questions in cluster chemistry. The systems reported in this article provide information about the influence that the ancillary ligands and the metal atoms themselves have upon the Lewis acid properties of the cluster. Attaining additional data on dirhodium(II) perfluorobutyrate provides information relevant to the former question, and the data on dimolybdenum(II) perfluorobutyrate provide information relevant to the latter.

Experimental Section

1. Synthesis and Purification. Metal Complexes. Rhodium acetate was prepared by literature methods.[3] Conversion to the perfluorobutyrate[4] involved the reflux of a solution of $Rh_2(\mathrm{acetate})_4$ in 30 mL of perfluorobutyric acid and 3 mL of perfluorobutyric anhydride for

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(1) R. S. Drago, S. P. Tanner, R. Richman, and J. R. Long, *J. Am. Chem. Soc.*, **101**, 2897 (1979).

(2) R. S. Drago, J. R. Long, and R. Cosmano, *Inorg. Chem.*, **20**, 2920 (1981). In this reference ϵ' and c' were used instead of k and k' of eq 1.

(3) P. Legzdins, R. W. Mitchell, A. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

(4) T. C. Kuechler, Ph.D. Thesis, University of Illinois, Urbana, IL, 1977.

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