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Vanishingly slow kinetics of the ClO_2/Cl^- reaction: its questionable significance in nonlinear chlorite reactions

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Contents

Abstract

There is considerable disagreement regarding the rate of the aqueous reaction $2ClO_2 + Cl^- + H_2O \rightarrow HClO_2 + ClO_2^- + HOCl$. Bray's early (1906) measurements indicate a third-order rate constant of 1×10^{-3} M^{-2} s^{-1} at 60°C, while recent kinetic modelling studies of chlorite oscillators use rate constants ranging from 5×10^1 to 8×10^7 M^{-2} s^{-1} at 25°C. We report attempts to make direct measurements on the reaction at 25°C. The reaction is very slow and photosensitive: in 0.1 M HCl with 0.8 mM ClO_2 less than 5% of the ClO_2 is

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consumed in 3 h, and in 0.01 M $HClO_4$/1 mM NaCl with 0.3 mM ClO_2 less than 10% is consumed in 2 weeks. Free energy calculations indicate that the reaction has an equilibrium constant too small for the reaction to occur by itself. In principle the reaction can be driven by the addition of product scavengers. Moreover, if appropriate scavengers are present to remove the purported intermediates $ClClO_2$ and ClO_2^- then the reaction could have the sought third-order rate law. Support for a finite but low rate constant ($k > 3.8 \times 10^{-5}$ M^{-2} s^{-1}) for this process comes from a consideration of a prior report on the kinetics of the reverse reaction in view of the principle of microscopic reversibility. Finally, ab initio calculations on $ClClO_2$, an intermediate in the reaction, lead to an upper limit of 1.2×10^{-5} M^{-2} s^{-1}; within the uncertainty in the hydration energy of $ClClO_2$, this result is in agreement with the lower limit given above. Thus, while an accurate value for the rate constant at 25°C is not yet in hand, it is clearly orders of magnitude less than has been used in several recent kinetic simulations.

Keywords: Chlorite; Nonlinear reactions; Slow kinetics

1. Introduction

The aqueous reaction of chlorite with thiocyanate ($ClO_2^- + SCN^-$) has been of interest since 1985, when it was reported to display sustained oscillations in a continuously-stirred tank reactor (CSTR) [1]. This reaction has also been shown to display chaos in a CSTR [2] and complex oligo-oscillatory behavior in batch [3,4]. Chlorine dioxide (ClO_2) is formed as an intermediate in this reaction, and its absorbance in the near-UV can be used as a convenient monitor of the oscillations [3,4]. Overall, the reaction mechanism is very complex, and a 24-step mechanism has been proposed for it [3].

One of the challenges in developing a mechanism for the ClO_2^-/SCN^- system is to devise a reaction scheme that can account for both the production and consumption of ClO_2. To this end, investigations of the related reaction of ClO_2 with SCN^- have been performed and analyzed by the Simoyi group [3]. Under conditions of excess SCN^- at pH 2, the loss of ClO_2 is autocatalytic; a subset mechanism consisting of only 21 steps was proposed to account for this behavior [3]. These mechanisms were used to obtain good-quality simulations of both reactions. In both mechanisms only two steps were included to account for the consumption of ClO_2:

$$ClO_2 + SCN^- \rightarrow ClO_2^- + SCN \quad k_1 = 2.01 \times 10^2 \tag{1}$$

$$2ClO_2 + Cl^- + H_2O \rightarrow HClO_2 + ClO_2^- + HOCl \quad k_2 = 5 \times 10^3 \tag{2}$$

Dimensions were not indicated for the rate constants, but it is reasonable to assume that k_1 is a second-order rate constant. There is ample precedent for the occurrence of reaction 1, as similar electron-transfer steps occur in the reactions of ClO_2 with I^-, N_3^-, and NO_2^- [5–7]. On the other hand, the dimensions of k_2 are less obvious, and one may question whether reaction 2 occurs at all.

Serious concerns about the rate constant for reaction 2 emerge when one examines other papers from Simoyi's group that discuss reactions involving ClO_2. Thus, in a study of the reaction of ClO_2^- with formaldehyde, a 13-step mechanism was used that included reaction 2 with a third-order rate constant of 5.0×10^1 M^{-2} s^{-1} [8]. In a study of the reaction of ClO_2^- with hydroxymethanesulfinic acid, reaction 2 was assigned a rate constant of 5×10^2 M^{-2} s^{-1} [9]. A rate constant of 8×10^7 M^{-2} s^{-1} was used for reaction 2 in a study of the reaction of ClO_2^- with formamidinesulfinic acid [10]. Most recently, a value of 100 M^{-2} s^{-1} was used in the mechanism for the reaction of hypotaurine with ClO_2^- [11]. As can be seen, values for k_2 spanning the range from 5.0×10^1 to 8×10^7 have been used in these simulations, and there is no clear indication that the correct value is being approached. It should be noted that determining an accurate value for k_2 was not the objective of these studies, and because of the great complexity of these reactions it would be very difficult to use them to make such a determination.

There are no published reports of a direct study of reaction 2 from Simoyi's group, but in two papers they cite prior studies of it [3,8]. In one of these papers, they cite the work of Kieffer and Gordon in support of reaction 2 [12]. In fact, Kieffer and Gordon reported only on the reverse of reaction 2. In the other paper they cite the work of Bray [13]. Bray's early study on reaction 2 showed that it proceeds exceedingly slowly at 0°C; at 60°C ($[H^+] = 0.006 - 0.6$ M) he obtained a rate constant of only 0.06 M^{-2} min^{-1}, or 1.0×10^{-3} M^{-2} s^{-1}. These results can hardly be construed as support for reaction 2 having a rate constant anywhere nearly as large as the smallest of those reported by Simoyi's group.

In the present paper we report direct measurements on reaction 2 at 25°C in an effort to provide a firmer basis for establishing the mechanisms of the reaction of ClO_2 with SCN^- and the reactions of ClO_2^- with SCN^-, formamidinesulfinic acid, hydroxymethanesulfinic acid, hypotaurine, and formaldehyde. Our analysis of these results, in combination with those of others, makes extensive use of the lessons so compellingly presented in Pearson's classic text, 'Kinetics and Mechanism' [14].

2. Experimental section

Stock solutions of aqueous ClO_2 (pH 2) were synthesized and characterized by procedures previously described [15]. Acids used in this study were purchased from Fischer (HCl (Certified ACS Plus, 12.1 M) and $HClO_4$ (75%)) and used without further purification. The NaCl was of reagent grade, purchased from Fischer, and used without further purification.

Reaction mixtures were prepared by measuring the appropriate quantity of ClO_2(aq.) via a gas-tight syringe fitted with a Teflon needle and diluting it tenfold or greater with prepared solutions of 0.1 M HCl (Exp. 1) and 0.01 M $HClO_4$/1.0 mM NaCl (Exp. 2 and 3) for a total volume of 3 ml. The reaction solutions were prepared in a cuvette, mixed, and placed in the sample compartment of the spectrophotometer for repetitive in situ spectral measurements. In Exp. 3 the reaction solution was prepared in a cell that was maintained at 25°C in the dark during the intervals between spectra. The data shown (Fig. 1) are typical results, but the individual experiments were repeated several times with good reproducibility.

Spectra were recorded by use of 1-cm quartz cells and a Hewlett–Packard 8453 diode array UV–vis spectrophotometer with a thermostated cell holder; the instrument was operated with both the UV and visible sources on, and an integration time of 0.5 s was used for each spectrum. Note that this instrument blocks the light beam with a shutter between spectra. Concentrations of ClO_2 were calculated from Beer's law with use of a value of 1200 M^{-1} cm^{-1} for the molar absorption of ClO_2 [15].

Kinetic simulations were performed with SPECFIT, which is designed to handle stiff systems of differential equations [16].

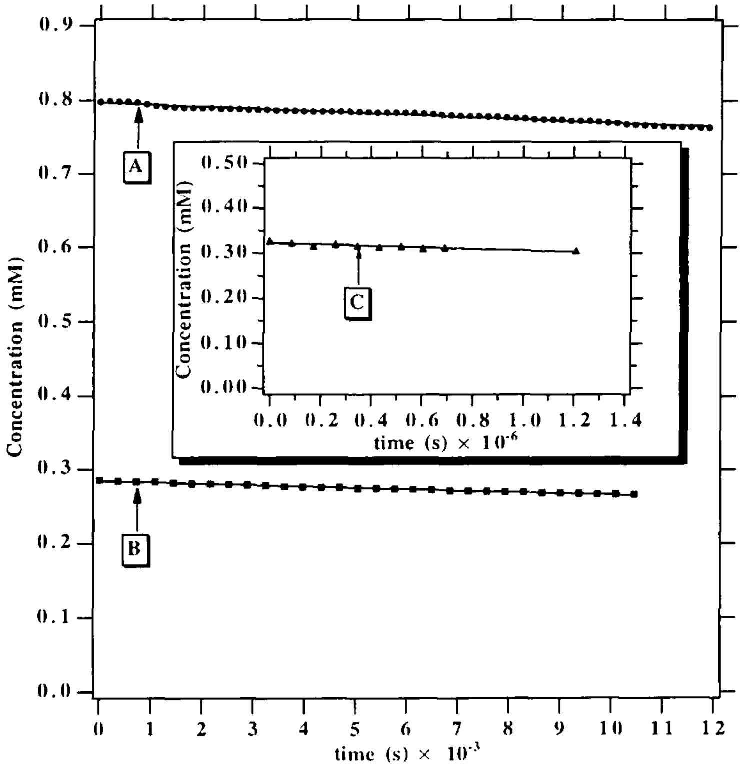

Fig. 1. Decay of ClO_2 in the presence of Cl^- as photochemically driven by the spectrophotometer light beam at 25°C. (A) $[ClO_2]_0 = 0.8$ mM in 0.10 M HCl, 3 min time intervals between scans. (B) $[ClO_2]_0 = 0.3$ mM in 1 mM Cl^- at pH 2.0 ($HClO_4$), 6 min time intervals between scans. (C) $[ClO_2]_0 = 0.3$ mM in 1 mM Cl^- at pH 2.0 ($HClO_4$), 24 h time intervals between scans. Subscript '0' indicates initial concentrations.

3. Results

As has been summarized elsewhere, the rate of ClO_2 disproportionation in mildly alkaline aqueous solutions is slow and subject to general base catalysis [17,18]. ClO_2 is quite stable in solutions that are not alkaline; for example, we find that solutions maintained in the dark at lowered temperatures (ca. 5°C) at pH 2.0 will show a loss of ClO_2 of $< 5\%$ over the course of 4 weeks.

In the present work we report studies on the stability of ClO_2 solutions at 25°C in acidic media with added chloride, conditions similar to those used in the prior studies of the ClO_2/SCN^- reaction. The loss of ClO_2 was monitored at 360 nm, the data being shown in Fig. 1. As can be seen, there is a small loss of ClO_2 that obeys zero-order kinetics during the time intervals examined; because of the slowness of the reaction, only a small fraction of the first half life was monitored. Fig. 1A shows the result obtained in 0.1 M HCl with 0.8 mM ClO_2, for which the initial rate is 2.7×10^{-9} M s^{-1} at 3 min scan^{-1}. Fig. 1B and C show results obtained in 0.01 M $HClO_4$/1.0 mM NaCl with 0.3 mM ClO_2, the two experiments differing in that the interval between spectra is 6 min in Fig. 1B and 24 h in Fig. 1C. Initial rates for these two experiments are 1.8×10^{-9} M s^{-1} at 6 min scan^{-1} and 1.7×10^{-11} M s^{-1} at 24 h scan^{-1}, respectively. The difference in rate between these last two experiments clearly shows that the monitoring beam of the instrument provides sufficient light intensity to drive the reaction photochemically. Solutions of ClO_2 are well known to be photochemically degraded [19]. It is by no means clear that any of our results pertain to thermal kinetics free of photochemical effects, and it is possible that they are entirely due to photochemistry. If the latter is the case, the rates should be proportional to the illumination time, as is roughly demonstrated by the two experiments in 0.01 M $HClO_4$; since the absorbances are rather high, a linear dependence on the concentration of ClO_2 cannot be expected.

If it is assumed that the loss of ClO_2 in these experiments is due to the thermal reaction 2, the measured initial rates lead to values for k_2 of 4.2×10^{-2} M^{-2} s^{-1} in 0.1 M HCl and 0.15 M^{-2} s^{-1} in 0.01 M $HClO_4$/1.0 mM NaCl at the lower scan rate. The latter conditions are typical of those used by Simoyi's group in its study of the ClO_2/SCN^- reaction [3]. There is considerable likelihood that our results are artificially accelerated by photochemical effects, especially for the first experiment. In view of these caveats, we consider that our results do not conflict with those of Bray [13]. Moreover, it is clear that reaction 2 either has a rate constant orders of magnitude less than any of those used in the various publications from Simoyi's group or else the reaction does not occur for thermodynamic reasons.

4. Discussion

4.1. Driving force calculation

An alternative perspective on reaction 2 can be developed by considering its thermodynamics. A value of $\Delta G^\circ = 71.2$ kJ mol^{-1} can be calculated for reaction 2 at 25°C by use of standard free energies of formation from the NBS tables [20]. This leads to an equilibrium constant K_2 of 3.4×10^{-13} for reaction 2. With an equilibrium constant of this magnitude, reaction 2 by itself cannot proceed to a significant degree under the conditions of our experiments. With the use of NBS data, the calculated value of K_2 is 5.0×10^{-12} at 60°C, the temperature of Bray's observations [13]. While this might appear to call into question Bray's results, he notes that the reaction is driven by conversion to the final products: ClO_3^- plus Cl^-. Thus, we have no reason to question Bray's results at 60°C, and, if a normal temperature dependence is assumed for k_2, then k_2 must be less than Bray's value of 1.0×10^{-3} M^{-2} s^{-1} at 25°C.

In view of the unfavorable equilibrium constant for reaction 2 at 25°C, our observations of the kinetics of loss of ClO_2 must either refer to some other process, such as its photochemical decomposition or physical loss through volatilization, or else the reaction is driven by formation of ClO_3^-. In such a situation the apparent measured rate constant may actually be lower than the true rate constant. This can occur if the reverse rate constant, k_{-2}, is sufficiently large, so that the system is maintained in a state of dynamic equilibrium that is thermodynamically unfavorable. If this were the case, then reaction 2 could be a significant pathway for ClO_2 loss in the ClO_2^- reactions investigated by Simoyi's group, provided that there is an effective means to drain off the products of reaction 2. Indeed, appropriate drain pathways exist in the proposed mechanisms, such as the reaction of HOCl with ClO_2^-.

4.2. *Isotopic tracer studies*

Isotopic exchange has been used as a test of whether reaction 2 can proceed via an unfavorable but dynamic equilibrium. Such experiments were performed by Dodgen and Taube in 1949 by use of Cl^*O_2 solutions labled with radioactive ^{38}Cl [21]. In their words, "Nothing in the chemistry of Cl^- and ClO_2 suggests that there is a rapid equilibrium which involves these as reactants, and some intermediate oxidation state as product. The experiments on Cl^- and ClO_2 mixtures... prove that such an equilibrium does indeed not exist." If it is assumed that reaction 2 provides a mechanism for chlorine exchange between ClO_2 and Cl^-, the data of Dodgen and Taube (Ref. [21] Exp. 18 of Table III) lead to an upper limit to k_2 of 0.09 M^{-2} s^{-1}. In a subsequent paper, Taube and Dodgen described similar experiments relating to the reverse of reaction 2: the reaction of radiolabled HOCl with ClO_2^- [22]. They found that the Cl^- product contained most of the active chlorine, from which they inferred an unsymmetrical transition state such as $Cl{-}ClO_2$. These results show that if reaction 2 occurs as a rapid but unfavorable equilibrium, it should not lead to exchange between Cl^- and ClO_2. As a result, the original experiments of Dodgen and Taube are uninformative regarding the rate of reaction 2.

4.3. *Kinetics of the reverse process*

The kinetics and mechanism of formation of ClO_2 via reaction 2 in reverse have been investigated at pH 5–6 by Peintler et al. [23]. Their mechanism, which is widely accepted, is as follows:

$$ClO_2^- + HOCl + H^+ \rightleftharpoons Cl_2O_2 + H_2O \quad k_3, k_{-3} \tag{3}$$

$$Cl_2O_2 + ClO_2^- \rightleftharpoons 2ClO_2 + Cl^- \quad k_4, k_{-4} \tag{4}$$

The overall reaction is

$$2ClO_2^- + HOCl + H^+ \rightleftharpoons 2ClO_2 + Cl^- \quad K_5 \tag{5}$$

These reactions are written as reversible processes for the purpose of further discussion, although in fact reaction 5 proceeds fully to the right. Peintler et al. found that the first step is rate limiting and that k_3 has a value of 1.06×10^6 M^{-2} s^{-1} at 25°C. Gordon and Tachiyashiki also investigated this reaction, and, although they dispute the importance of reaction 4, a value of 5.7×10^6 M^{-2} s^{-1} for k_3 can be derived from their results [24]. The disagreement between these results apparently is due to unrecognized general acid catalysis [25]. The principle of detailed balancing requires that, if the forward reaction at equilibrium has k_3 as the rate-limiting step, then the reverse process at equilibrium has the rate law

$$\frac{d[ClO_2]}{dt} = \frac{k_{-4}k_{-3}[ClO_2]^2[Cl^-]}{k_4[ClO_2^-]} \tag{6}$$

Thus, if an appropriate drain pathway exists that can drive reaction 5 in its reverse direction, the rate law under the conditions of Peintler et al. would not be expected to conform to the simple third-order process implied by reaction 2.

On the other hand, the reverse of reaction 4 could become rate limiting if ClO_2^- or the intermediate $ClClO_2$ were scavenged by some other species present in solution; in strongly acidic media H^+ could fill this role as a ClO_2^- scavenger. The rate law would be indistinguishable from that proposed for reaction 2:

$$\frac{d[ClO_2]}{dt} = k_{-4}[ClO_2]^2[Cl^-] \tag{7}$$

The data of Peintler et al. imply a lower limit for the value of k_{-4}. This can be seen as follows. If the steady-state approximation is applied to the reaction of ClO_2^- with HOCl the following rate law is obtained:

$$\frac{d[ClO_2]}{dt} = \frac{k_3k_4[HOCl][ClO_2^-]^2[H^+]}{k_4[ClO_2^-] + k_{-3}} \tag{8}$$

Rate law 8 simplifies to the observed rate law when $k_4[ClO_2^-] \gg k_{-3}$. Under the conditions of the experiments of Peintler et al. this inequality leads to $k_{-3}/k_4 \ll 10^{-4}$ M. According to the principle of microscopic reversibility, $K_5 = k_3k_4/(k_{-3}k_{-4})$. NBS data yield a value of 2.8×10^{14} M^{-1} for K_5. Using our calculated value for K_5, the measured value of k_3, and the above inequality leads to a *lower* limit of 3.8×10^{-5} M^{-2} s^{-1} for k_{-4} at 25°C. As is noted above, Peintler et al. overlooked the fact that reaction 5 is subject to general acid catalysis, and thus the value of k_3 is probably somewhat too high. Correction for this omission would give a smaller value for the lower limit to k_{-4} than 3.8×10^{-5} M^{-2} s^{-1}.

4.4. Energetics of $ClClO_2$

Support for a low value for k_{-4} can be obtained from a consideration of the energetics of the intermediate, $ClClO_2$. This species has been synthesized [26], and it has also been detected as an intermediate in aqueous solution [27]. Its structure has been determined by rotational spectroscopy, which indicates a pyramidal geometry at the central chlorine atom [28]. Ab initio G-2 calculations yield a value of 154.2 kJ mol^{-1} for $\Delta_f H^\circ_{298}$ for the gas-phase molecule [29]. We find that AM1 calculations give a value of 299 J K^{-1} mol^{-1} for S° for this species, such that $\Delta_f G^\circ = 193$ kJ mol^{-1} for gas phase $ClClO_2$. If we estimate that $\Delta_{hyd} G^\circ = 0$ for this molecule (as for ClO_2) and we use appropriate NBS data, we calculate that $\Delta G^\circ = -101$ kJ mol^{-1} for reaction 4. Thus, the reverse process has $\Delta G^\ddagger > 101$ kJ mol^{-1}; from the relationship $k = (RT/Nh)\exp(-\Delta G^\ddagger/RT)$ we find that k_{-4} is less than 1.2×10^{-5} M^{-2} s^{-1}. The largest likely source of error in this result is in the estimate of $\Delta_{hyd} G^\circ$ for $ClClO_2$, which could easily be in error by 10 kJ mol^{-1}. To the degree that hydration of $ClClO_2$ is more favorable, the estimated value of k_{-4} will increase. As a consequence, there is no significant contradiction between this estimate and that obtained from Eq. (8).

4.5. Analysis of prior mechanisms

In principle, it would be appropriate to determine whether the simulation of the autocatalytic kinetics of the reaction of ClO_2 with SCN^- as reported by Chinake et al. [3] is affected by use of a realistic value for k_2. Unfortunately, we find that we are unable to reproduce their simulated results (see Ref. [3] Fig. 8A) when we use their mechanism and rate constants. That this failure is due to a fundamental shortcoming of the mechanism rather than to our numerical integration methods can be seen from the following considerations: Their proposed mechanism contains no steps that generate ClO_2, and the only steps that consume ClO_2 are those shown above in reactions 1 and 2. Under their initial conditions of $[ClO_2] = 0.76$ mM, $[SCN^-] = 1$ mM, $[H^+] = 0.02$ M and $[Cl^-] = 0.0$ mM the calculated initial rate with their value for k_1 is 1.5×10^{-4} M s^{-1}. The rate increment due to reaction 2 at the first half-life is, at maximum 2.7×10^{-7} M s^{-1} with their value of k_2, if all of the consumed ClO_2 is converted to Cl^-. These calculations clearly demonstrate that significant autocatalysis is impossible with the given mechanism and rate constants; we infer that there is some unknown typographic error in the mechanism or set of rate constants.

Although we have not performed calculations on the kinetics of the chlorite reactions with formaldehyde, hydroxymethanesulfinic acid, formamidinesulfinic acid, and hypotaurine, some comments regarding potential pH effects are in order. The reaction of formamidine sulfinic acid [10] was studied under pH conditions similar to those for the SCN^- reaction, and hence our results bear directly on that work. In that study a rate constant of 8×10^7 M^{-2} s^{-1} was used for k_2. However, since ClO_2 is a reactant in several other steps having adjustable rate constants, it is conceivable that the effects of using a realistic value for k_2 could be accommodated by appropriate adjustment of other rate constants. The reaction of hypotaurine was likewise studied under acidic conditions [11], and a value of 100 M^{-2} s^{-1} was used for k_2. In this case, however, a revised mechanism is required, because the current mechanism specifies forward and reverse rate laws for reaction 2 that violate the principle of detailed balancing. The significance of our results to the mechanisms of the formaldehyde [8] and hydroxymethanesulfinic acid [9] reactions is less clear, since they were studied at higher pH.

5. Conclusions

In summary, direct determination of the magnitude of k_2 at 25°C presents great difficulties because the reaction is very slow, thermodynamically unfavorable, and suffers from side reactions such as disproportionation and photochemistry. At present, the best estimate is that the rate constant should be less than the value of 1.0×10^{-3} M^{-2} s^{-1} as determined by Bray at 60°C, greater than about 3.8×10^{-5} M^{-2} s^{-1} as determined from analysis of the kinetics of the reverse reaction at 25°C and less than 1.2×10^{-5} M^{-2} s^{-1} as required by the energetics of the $ClClO_2$ intermediate. In any case, the value of k_2 is orders of magnitude less than that used in the various kinetic schemes from Simoyi's group for the reactions of ClO_2 with SCN^- or of ClO_2^- with SCN^-, formamidinesulfinic acid, hydroxymethanesulfinic acid, formaldehyde, and hypotaurine.

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