

decomposition of the acyl (COR) nor further reaction with H<sub>2</sub> to form RCHO takes place. The presence of a Rh-O-Si bond would stabilize the Rh dimer structure on the SiO<sub>2</sub> surface and assures the reversible metal-assisted formation and decomposition of acyl group in the SiO<sub>2</sub>-attached Rh dimers.

The present work demonstrated that the CO-insertion reaction, which is a key step in ethene hydroformylation, is promoted by metal-metal interaction at the metal surface. Another type of the promotion of CO insertion through the direct bonding of CO molecules with Lewis acids added as cocatalyst (metal-CO-Lewis acid) has been proposed.<sup>44,45</sup> However, the metal-assisted CO-insertion mechanism proposed here is essentially different from that the Lewis-acid promoter effects. The metal-assisted mechanism would be the other case to explain the role of metal ensembles in metal catalysis.

The new Rh dimer catalyst was a selective catalyst for ethene hydroformylation as compared with a usual impregnation Rh catalyst as shown in Table V. The activity for the hydrogenation of ethene to form ethane was similar to that of the impregnation catalyst (TOF =  $9.9 \times 10^{-4} \text{ min}^{-1}$  at 413 K), while the formation of propanal on the Rh dimer catalyst was enhanced by a factor of 30 as compared with the impregnation catalyst. The hydro-

formylation reaction involves three important elementary reaction steps, CO adsorption, CO insertion, and hydrogenation, as shown in Figure 5. The initial rates of each step could be determined by the changes of IR peaks for CO (1969 cm<sup>-1</sup>) and acyl (1710 cm<sup>-1</sup>) groups as shown in Figure 7. The TOF for each step decreased in the order CO adsorption to form twin carbonyls ( $2 \times 10^{-1} \text{ min}^{-1}$  at 313 K) > CO insertion to form acyl group ( $8.3 \times 10^{-2} \text{ min}^{-1}$  at 423 K) > hydrogenation to form propanal ( $1.0 \times 10^{-2} \text{ min}^{-1}$  at 423 K). The steady-state overall reaction rate for propanal formation was much lower than the rates of the three reaction steps. The transformation between species C and species E is reversible, as proved by the observation of IR spectra at various CO pressures. The concentration of intermediate C under catalytic reaction conditions is estimated to be about 3% of the total Rh atoms.

The present combination study of in situ EXAFS and in situ FT-IR techniques revealed the dynamic change of the structure of Rh dimers on the SiO<sub>2</sub> surface during the course of ethene hydroformylation. The chemically designed metal catalysts provide molecular level information on the genesis of essential factors for metal catalysis and, hence, basic implications for developments of new types of catalysts.

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## Experimental and Modeling Study of Oscillations in the Chlorine Dioxide-Iodine-Malonic Acid Reaction<sup>1</sup>

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**Abstract:** At pH 0.5–5.0, a closed system containing an aqueous mixture of chlorine dioxide, iodine, and a species such as malonic acid (MA) or ethyl acetoacetate, which reacts with iodine to produce iodide, shows periodic changes in the light absorbance of I<sub>3</sub><sup>-</sup>. This behavior can be modeled by a simple scheme consisting of three component reactions: (1) the reaction between MA and iodine, which serves as a continuous source of I<sup>-</sup>; (2) the reaction between ClO<sub>2</sub><sup>\*</sup> and I<sup>-</sup>, which acts as a source of ClO<sub>2</sub><sup>-</sup>; and (3) the self-inhibited reaction of chlorite and iodide that kinetically regulates the system. The fast component reaction between chlorine dioxide and iodide ion was studied by stopped-flow spectrophotometry. The rate law is  $-[ClO_2^*]/dt = 6 \times 10^3 \text{ (M}^{-2} \text{ s}^{-1})[ClO_2^*][I^-]$ . A two-variable model obtained from the empirical rate laws of the three component reactions gives a good description of the dynamics of the system. The oscillatory behavior results not from autocatalysis but from the self-inhibitory character of the chlorite-iodide reaction.

### Introduction

The reaction between iodide ion and chlorite ion exhibits a remarkable variety of kinetic phenomena. These include bistability and oscillatory behavior in a continuous-flow stirred-tank reactor (CSTR),<sup>3</sup> propagating waves in excitable media,<sup>4</sup> stirring and mixing effects on the behavior in a CSTR,<sup>5</sup> critical slowing down,<sup>6</sup>

and stochastic behavior.<sup>7</sup> By introducing an additional reactant that can react to regenerate the iodide consumed during each cycle of oscillation, De Kepper et al.<sup>8</sup> constructed the chlorite-iodate-thiosulfate and the chlorite-iodide-malonic acid (MA) systems, which oscillate in a closed (batch) as well as in an open (flow, CSTR) system. Ouyang<sup>9</sup> has carried out a detailed experimental study of the ClO<sub>2</sub><sup>-</sup>-I<sup>-</sup>-MA reaction. Recently, this reaction has been found to show<sup>10</sup> the symmetry-breaking, reaction-diffusion structures predicted by Turing<sup>11</sup> nearly 40 years ago.

(1) Systematic Design of Chemical Oscillators. 67. Part 66: Simoyi, R. H.; Manyonda, M.; Masere, J.; Mtambo, M.; Ncube, I.; Patel, H.; Epstein, I. R.; Kustin, K. *J. Phys. Chem.*, in press.

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Significant effort has been made to describe the behavior found in a flow reactor,<sup>12-14</sup> and the mechanism developed by Citri and Epstein<sup>14</sup> (CE) has been quite successful in describing the oscillations. Relatively little attention, however, has been devoted to the mechanism of the batch oscillations in the  $\text{ClO}_2^-$ - $\text{I}^-$ -MA reaction, despite its key role in the development of open reactors<sup>15</sup> for studying spatial pattern formation and the discovery of the first Turing structures<sup>10</sup> in this system.

We have found that a simple extension of the CE mechanism to include the malonic acid-iodine reaction cannot account for the oscillation in batch. We arrived at the conclusion that one or more essential species and their reactions, which are negligible in the CSTR, must be important in batch. In the batch oscillation,  $[\text{ClO}_2^-]_0$  always exceeds  $[\text{I}^-]_0$ , while in the flow system the ratio of  $[\text{ClO}_2^-]_0$  to  $[\text{I}^-]_0$  is typically 1/3 for oscillation. The earlier mechanistic studies did not take into consideration the formation of  $\text{ClO}_2^*$  in the chlorite-iodide reaction, since the rate of the spontaneous disproportionation of chlorite ion (the assumed source of chlorine dioxide) is negligible in comparison to the rates of other component reactions when  $\text{I}^-$  is in excess. The possible role of the  $\text{ClO}_2^*$  radical in chlorite-based oscillators was suggested first by Epstein and Orbán.<sup>16</sup> Later, Rábai and Beck<sup>17</sup> demonstrated experimentally that the disproportionation of  $\text{ClO}_2^-$  to  $\text{ClO}_2^*$  and  $\text{Cl}^-$  is accelerated by the intermediates of the  $\text{I}_2$ - $\text{ClO}_2^-$  reaction and that the formation rate of  $\text{ClO}_2^*$  can be comparable to the rate of the fast chlorite-iodine reaction.

With these considerations in mind, we examined the possible role of  $\text{ClO}_2^*$  in the batch oscillator and discovered that chlorine dioxide and iodine formed in the preoscillatory period are responsible, along with the malonic acid, for the oscillation. This finding enables us to construct a new batch oscillator, chlorine dioxide-iodine-malonic acid. In a recent communication,<sup>18</sup> we presented experimental evidence for the critical role of  $\text{ClO}_2^*$  and proposed a simple model for the oscillation. In the present paper, we report the detailed experimental investigation and modeling of this oscillator.

## Experimental Section

**Materials.** Sodium chlorite was purified as described earlier,<sup>19</sup> and stock solutions were kept in the dark. Solutions were discarded when a pale yellow color indicated the decomposition of  $\text{ClO}_2^-$ . Chlorine dioxide was prepared from potassium chlorate and oxalic acid in sulfuric acid<sup>20</sup> and was purified by bubbling through saturated sodium carbonate solution to remove  $\text{CO}_2$  as well as traces of  $\text{HCl}$  and  $\text{Cl}_2$ . The purified chlorine dioxide gas was dissolved in ice-cold water. Stock solutions of  $\text{ClO}_2^*$  were acidified to pH 3-4 and were stored in darkness at 5 °C. The  $\text{ClO}_2^*$  concentration was determined by spectrophotometry ( $\epsilon = 1265 \text{ cm}^{-1} \text{ M}^{-1}$  at 360 nm).<sup>21</sup> All other chemicals were the highest purity commercially available and were used as received.

**Methods.** The reaction was started by injecting a small volume of one of the reactants into a mixture containing the other components in a stirred spectrophotometric cell. The mixing time is about 1-2 s. Spectrophotometric measurements were performed in an HP8452A UV-vis diode array spectrophotometer equipped with a thermostated cell holder and magnetic stirrer. A complete spectrum of the reaction mixture could be obtained each second of the reaction time (a single spectrum requires 0.1 s to measure, which is much shorter than the time scale of the chemical changes in the reaction). In most cases, absorbances at two to six different wavelengths were used for analysis. All measurements were

performed at 25 °C, and the stirring rate in the spectrophotometric cell was 400 rpm.

The kinetics of the fast reaction between chlorine dioxide and iodide ion were studied separately in a stopped-flow spectrophotometer (HI-TECH SF-3L) at 468 nm (the isosbestic point of  $\text{I}_2$  and  $\text{I}_3^-$  ( $\epsilon = 740 \text{ cm}^{-1} \text{ M}^{-1}$ )) and at 353 nm ( $\epsilon_{\text{I}_3^-} = 26400 \text{ cm}^{-1} \text{ M}^{-1}$ ).<sup>21</sup>

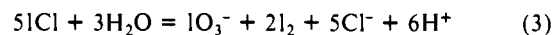
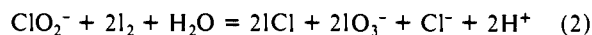
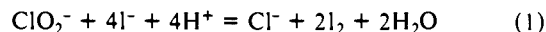
## Results

**Chlorite-Iodide-Malonic Acid Oscillator.** There have been, to our knowledge, two previous studies of the oscillatory behavior of the  $\text{ClO}_2^-$ - $\text{I}^-$ -MA reaction. De Kepper et al.<sup>8</sup> employed relatively high initial concentrations, which resulted in precipitation of iodine. Ouyang<sup>9</sup> worked with more dilute reaction mixtures and obtained more reproducible results.

We first studied the role of the starch indicator used by both groups. Although starch affects the period and the amplitude and modifies the range of initial concentrations under which oscillations take place, its presence is not crucial for the phenomenon to occur. We found oscillations at several of Ouyang's compositions in the absence of starch. The stability, molar absorbance, and stoichiometry of the starch-triiodide complex depend upon the structure of the starch molecules.<sup>22</sup> We prefer to investigate the system without starch, because the behavior is then more reproducible and simpler for both experimental and mechanistic studies. The starch-free oscillation is not visible. It can be monitored, however, spectrophotometrically at the wavelengths of triiodide absorbance.

The appearance of the oscillation depends critically on the ratio  $[\text{ClO}_2^-]_0/[\text{I}^-]_0$ . Oscillations are found when this ratio is between 1.25 and 1.54 at the following initial concentrations:  $[\text{ClO}_2^-]_0 = 5.7 \times 10^{-3}$ ,  $[\text{I}^-]_0 = (3.7-4.6) \times 10^{-3}$ ,  $[\text{MA}]_0 = 1.0 \times 10^{-3}$ , and  $[\text{H}_2\text{SO}_4]_0 = 3.8 \times 10^{-3} \text{ M}$  when no starch is added. In the presence of starch (1 g/L), oscillations are visible only when the ratio lies in the range 1.25-1.33. The occurrence of oscillation is less sensitive to the initial concentration of malonic acid. At  $[\text{ClO}_2^-]_0 = 5.7 \times 10^{-3}$ ,  $[\text{I}^-]_0 = 4.3 \times 10^{-3}$ , and  $[\text{H}_2\text{SO}_4]_0 = 3.8 \times 10^{-3} \text{ M}$ ,  $[\text{MA}]$  can be varied from  $6.4 \times 10^{-4}$  to at least  $4.0 \times 10^{-3} \text{ M}$  (at higher  $[\text{MA}]$  the changes are too rapid to be measured quantitatively, but oscillation almost certainly occurs).

The oscillation is always preceded by a preoscillatory or induction period. In order to understand the oscillation, an analysis of the products of the preoscillatory period is necessary. Since we can follow the reaction simultaneously at many different wavelengths, we have been able to identify the stable intermediates and products and to calculate their concentrations during the reaction. In the preoscillatory period, the change observed in iodine concentration is similar to that found in the chlorite-iodide reaction in the absence of malonic acid.<sup>13</sup> We observe an autocatalytic increase followed by a sharp decrease and a slow regeneration of iodine:

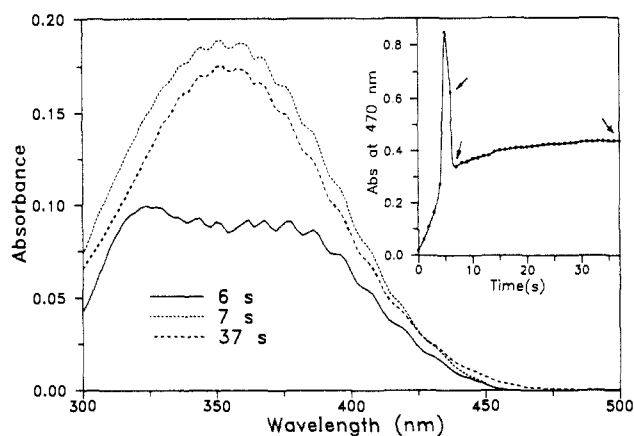


This similarity suggests that the reaction between  $\text{ClO}_2^-$  and  $\text{I}^-$  has ended before the oscillation starts. We infer that one or more of the products generated in the consumption of the initial reactants plays a crucial role in the subsequent periodic behavior. Reaction 2 is always accompanied by the formation of chlorine dioxide.<sup>17</sup> Chloride ion, iodate ion, iodine, and chlorine dioxide appear as the relatively stable products of the preoscillatory phase and as potential candidates for the key role in the oscillatory stage. Since  $\text{Cl}^-$  is kinetically sluggish and its only role under these conditions is to retard the disproportionation of  $\text{ICl}$  (or of  $\text{IOH}$ , which is in rapid equilibrium with  $\text{ICl}$  in acidic aqueous solution), we do not consider it further.

Iodate ion can react with  $\text{I}^-$  to yield  $\text{I}_2$  in acidic solution, and thus  $\text{IO}_3^-$  might be an important participant in the oscillation.

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**Figure 1.** Spectra of a reaction mixture with  $[\text{ClO}_2^*]_0 = 5.71 \times 10^{-3}$ ,  $[\text{I}^-]_0 = 4.29 \times 10^{-3}$ , and  $[\text{H}_2\text{SO}_4]_0 = 3.8 \times 10^{-3}$  M at different reaction times (see arrows in inset) after the spectra of  $\text{I}_3^-$  and  $\text{I}_2$  are subtracted.

We can calculate the  $[\text{IO}_3^-]$  formed using the stoichiometry of eqs 2 and 3. We determined  $[\text{I}_2]$  in the mixture at the start of the oscillation from the absorbance at 468 nm, where no other species present absorbs light. The concentration of  $\text{ClO}_2^*$  generated can be estimated from the spectra of the reaction mixture. Spectra after subtracting the contributions of  $\text{I}_3^-$  and  $\text{I}_2$  are shown in Figure 1 at three different reaction times. No chlorine dioxide is detected in the initial portion of the reaction while iodide is still present. The characteristic spectrum of  $\text{ClO}_2^*$  appears in the second stage of the reaction simultaneously with the sharp decrease in iodine concentration. During the partial regeneration of  $\text{I}_2$ ,  $[\text{ClO}_2^*]$  remains almost unchanged. The concentration of chlorine dioxide calculated from the absorbance measured at 360 nm is about  $2 \times 10^{-4}$  M at the beginning of the oscillation.

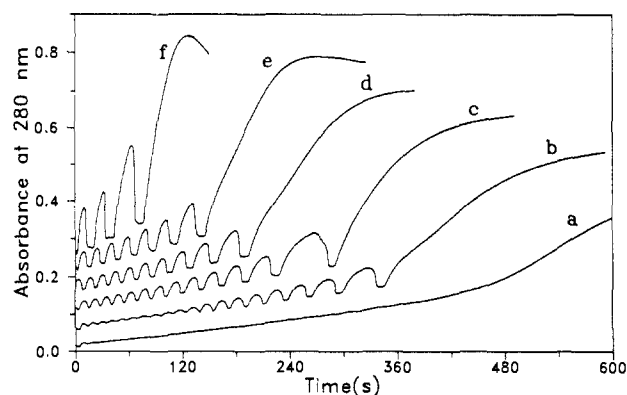
If we mix the products of the chlorite-iodide reaction at their calculated concentrations ( $[\text{IO}_3^-]_0 = 3.1 \times 10^{-3}$ ,  $[\text{I}_2]_0 = 5.1 \times 10^{-4}$ ,  $[\text{ClO}_2^*]_0 = 2 \times 10^{-4}$  M) with malonic acid ( $[\text{MA}]_0 = 1 \times 10^{-3}$ ) and sulfuric acid ( $[\text{H}_2\text{SO}_4]_0 = 5 \times 10^{-3}$  M) to maintain the acidic pH, oscillation begins immediately. Further study reveals that *oscillation occurs even if no iodate ion is added to the mixture, but omitting any of the other components eliminates oscillation*. Therefore, besides malonic acid, *only chlorine dioxide and iodine are needed for oscillation*. In order to elucidate this behavior, we next investigated the  $\text{ClO}_2^*-\text{I}_2$ -MA system.

**Chlorine Dioxide-Iodine-Malonic Acid Oscillator.** A reaction mixture containing  $\text{ClO}_2^*$ ,  $\text{I}_2$ , and MA behaves much like the  $\text{ClO}_2^*-\text{I}^-$ -MA system. Both systems exhibit batch oscillations, but the former reaction has no preoscillatory period. On mixing the reactants, oscillation starts immediately with small amplitude. Only the very high molar absorbance of  $\text{I}_3^-$  (and/or that of the triiodide-starch complex) allows observation of this behavior. Surprisingly, the amplitude grows until the oscillation suddenly ceases. Both the amplitude and the number of oscillations depend upon the initial concentrations; the higher the amplitude the fewer oscillations are observed.

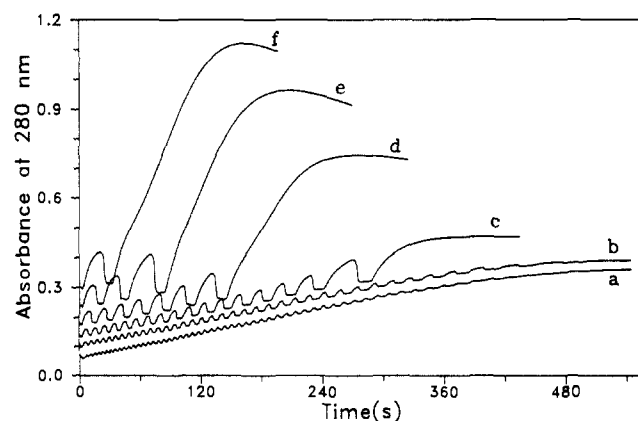
The effect of malonic acid concentration is shown in Figure 2. Oscillations were found when  $4 \times 10^{-3} > [\text{MA}]_0 > 4.5 \times 10^{-4}$  M. When  $[\text{MA}]_0 = 4.8 \times 10^{-4}$  M (Figure 2, curve b) oscillation starts with decreasing amplitude, but then after several periods the amplitude begins to increase.

Since malonic acid reacts with iodine to yield iodide ion, we assumed that the role of MA is to supply  $\text{I}^-$  at a moderate rate. If this hypothesis is true, other organics that react in a similar fashion with iodine should also be capable of generating oscillations. We find that oscillatory behavior occurs if we replace malonic acid by ethyl acetoacetate.

Iodide ion can, of course, be supplied not only by a chemical reaction but also by an external input flow. We might therefore expect chlorine dioxide and iodide ion to react with oscillatory kinetics in a flow reactor even without the addition of malonic acid. Our experiments show oscillation in  $\text{ClO}_2^*-\text{I}^-$  systems in a CSTR over a surprisingly broad range of input concentrations



**Figure 2.** Oscillatory curves at several malonic acid concentrations (M) in the  $\text{ClO}_2^*-\text{I}^-$ -MA system:  $[\text{ClO}_2^*]_0 = 1.0 \times 10^{-4}$ ;  $[\text{I}_2]_0 = 5.0 \times 10^{-4}$ ;  $[\text{H}_2\text{SO}_4]_0 = 5.0 \times 10^{-3}$ ;  $[\text{MA}]_0 = 4.0 \times 10^{-4}$  (a),  $4.8 \times 10^{-4}$  (b),  $6.0 \times 10^{-4}$  (c),  $7.4 \times 10^{-4}$  (d),  $1.0 \times 10^{-3}$  (e),  $2.0 \times 10^{-3}$  (f). Successive curves are shifted up by 0.05 absorbance unit for better viewing, since in the absence of a shift the curves overlap.



**Figure 3.** Oscillatory curves at several chlorine dioxide concentrations (M) in the  $\text{ClO}_2^*-\text{I}_2$ -MA system:  $[\text{I}_2]_0 = 5.2 \times 10^{-4}$ ;  $[\text{MA}]_0 = 1.0 \times 10^{-3}$ ;  $[\text{H}_2\text{SO}_4]_0 = 5 \times 10^{-3}$ ;  $[\text{ClO}_2^*]_0 = 4.3 \times 10^{-4}$  (a),  $2.8 \times 10^{-4}$  (b),  $1.7 \times 10^{-4}$  (c),  $1.0 \times 10^{-4}$  (d),  $7.1 \times 10^{-5}$  (e),  $5 \times 10^{-5}$  (f). Successive curves are shifted as in Figure 2.

and residence time. A typical oscillatory reaction mixture contains  $[\text{ClO}_2^*]_0 = 1 \times 10^{-4}$  M,  $[\text{I}^-]_0 = 1 \times 10^{-4}$  M, and  $[\text{H}_2\text{SO}_4]_0 = 5 \times 10^{-3}$  M at a reciprocal residence time  $k_0 = 5 \times 10^{-3}$  s $^{-1}$ . The oscillations were monitored with an iodide-selective electrode.

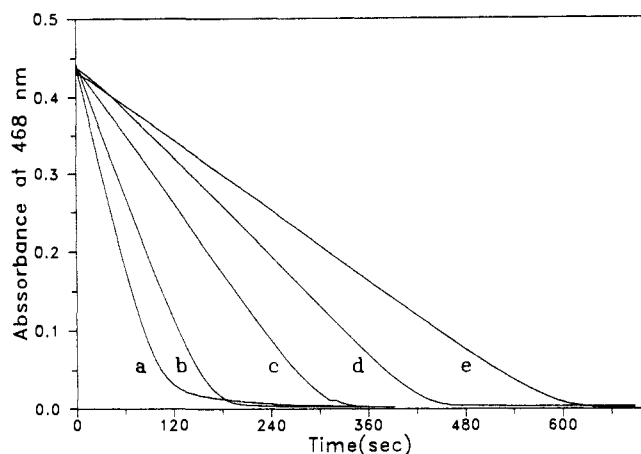
The effect of  $[\text{ClO}_2^*]$  in this system is shown in Figure 3. Oscillations are found if  $6 \times 10^{-5} \leq [\text{ClO}_2^*]_0 \leq 6 \times 10^{-4}$  M. The amplitude decreases with increasing  $[\text{ClO}_2^*]_0$ . At concentrations above  $6 \times 10^{-4}$  M, the amplitude of oscillation is too small ( $<0.002$  absorbance unit) to be observed unambiguously, but it is difficult to say exactly where the oscillatory behavior ceases.

With  $[\text{ClO}_2^*]_0 = 1.0 \times 10^{-4}$ ,  $[\text{MA}]_0 = 1.0 \times 10^{-3}$  M, and  $[\text{H}_2\text{SO}_4]_0 = 5.0 \times 10^{-3}$  M, oscillations occur for  $1.0 \times 10^{-4} \leq [\text{I}_2]_0 \leq 8 \times 10^{-4}$  M. At the low end of this range, only about three to four oscillations take place with amplitude decreasing in time. We were unable to investigate higher concentrations of iodine because the solubility of  $\text{I}_2$  is  $1.1 \times 10^{-3}$  M.

#### Component Reactions of the $\text{ClO}_2^*-\text{I}_2$ -MA Oscillator

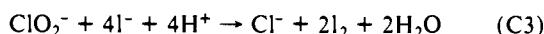
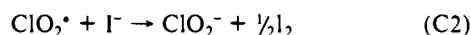
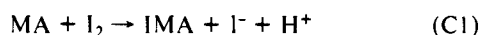
We now consider how the components of the chlorine dioxide-iodine-malonic acid system may interact. Rábai and Beck<sup>17</sup> have demonstrated experimentally that  $\text{ClO}_2^*$  does not react with  $\text{I}_2$ . We investigated the reaction between chlorine dioxide and malonic acid and found it to be very slow. The half-life of  $\text{ClO}_2^*$  in a reaction mixture with  $[\text{MA}]_0 = 0.05$  M and  $[\text{ClO}_2^*]_0 = 1.0 \times 10^{-3}$  M at 25 °C is about 2 h. Our experiments show that the spontaneous formation of  $\text{ClO}_2^*$  in acidic chlorite solution is not accelerated by malonic acid, indicating that the direct reaction between  $\text{ClO}_2^*$  and MA cannot be fast.

The time scale of the oscillation is a few minutes. Therefore, we neglected the above reactions and took into consideration only



**Figure 4.** Iodine consumption in the reaction between malonic acid and iodine at several pH values:  $[I_2]_0 = 5.9 \times 10^{-4}$ ;  $[MA]_0 = 2.0 \times 10^{-3}$  M; pH 2.76 (a), 3.24 (b), 3.76 (c), 4.35 (d), 4.86 (e). The pH was adjusted with 0.1 M  $H_3PO_4/Na_2PO_4$  (a-c) and 0.1 M acetate buffer (d, e).

the following three component reactions: the iodination of malonic acid (C1) as a continuous source of  $I^-$ ; the reaction of chlorine



dioxide with iodide ion (C2), which provides  $ClO_2^-$ ; and finally the reaction (C3) between the  $I^-$  formed in reaction (C1) and the  $ClO_2^-$  formed in reaction (C2).

**Iodine-Malonic Acid Reaction.** The kinetics of the reaction (C1) between  $I_2$  and MA have been investigated by Leopold and Haim.<sup>23</sup> They studied the reaction at low  $[I_2]$  and high  $[I^-]$  and found first-order kinetics with respect to iodine. Their mechanism involves the enolization of malonic acid, which is followed by a relatively fast reaction between iodine and the enol form. Because the rate is limited by the amount of enol present, at high iodine concentrations the rate becomes zero order in iodine.

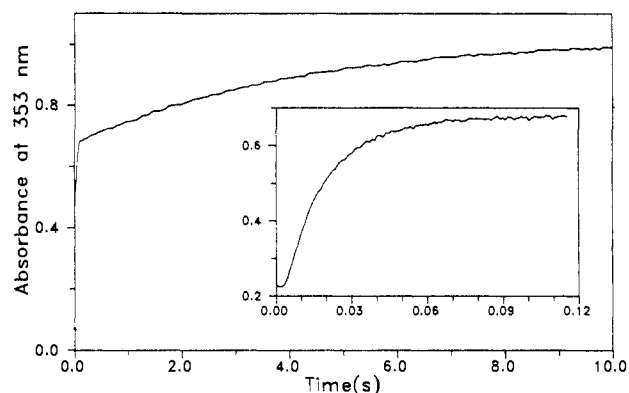
De Kepper and Epstein<sup>24</sup> used a simple rate law for reaction C1 that is valid at low pH. As we show later, this reaction is the only one of the three component processes whose kinetics depends on the concentration of hydrogen ion. Since no kinetic data were found in the literature under the conditions of our experiments (high  $[I_2]$ , low  $[I^-]$ , pH 2-5), we studied the effect of pH on the reaction. Figure 4 shows the iodine consumption in the  $I_2$ -MA reaction at several pH's. The reaction is zero order in iodine up to 90% conversion. The rate is independent of pH if  $[H^+] > 1 \times 10^{-2}$  M. At pH 5 the reaction is about 10 times slower than at pH 2. Consequently, if we increase  $[MA]_0$  to compensate for this decrease in rate, we can maintain oscillations at pH 5 as well. Oscillations were found experimentally from pH 0.35 to 5 with the following initial concentrations:  $[ClO_2^*]_0 = 1.0 \times 10^{-4}$ ,  $[I_2]_0 = 5.0 \times 10^{-4}$ ,  $[MA]_0 = 6 \times 10^{-4}$ ,  $[H_2SO_4]_0 = 0.2$  M at pH 0.35 and  $[ClO_2^*]_0 = 2.0 \times 10^{-4}$ ,  $[I_2]_0 = 5.0 \times 10^{-4}$ ,  $[MA]_0 = 1 \times 10^{-2}$  M at pH 5. The pH was adjusted to 5 with 0.2 M acetate buffer. At higher pH's no oscillations were found, probably because the  $I^-$  generated from the hydrolysis of iodine is then sufficient to suppress the oscillation.

Our rate equation for reaction C1 is

$$-d[I_2]/dt = k_{1a}[MA][I_2]/(k_{1b} + [I_2]) \quad (R1)$$

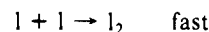
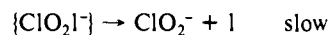
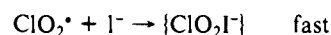
with  $k_{1a} = 5 \times 10^{-3} s^{-1}$ ,  $k_{1b} = 5 \times 10^{-5}$  M at pH 2 and  $k_{1a} = 4 \times 10^{-4} s^{-1}$ ,  $k_{1b} = 5 \times 10^{-5}$  M at pH 5.

**Chlorine Dioxide-Iodide Ion Reaction.** The reaction between  $ClO_2^*$  and  $I^-$  was used in the analytical determination of chlorine dioxide by Bray.<sup>25</sup> The kinetics of the reaction were studied in



**Figure 5.** Typical stopped-flow kinetic curve in the  $ClO_2^*-I^-$  reaction:  $[ClO_2^*]_0 = 1.0 \times 10^{-4}$ ,  $[I^-]_0 = 2.0 \times 10^{-2}$ ,  $[H^+]_0 = 1.0 \times 10^{-2}$  M. The inset shows the first (fast) part of the reaction on an extended time scale.

excess iodide by use of a rapid-mixing syringe device by Fukutomi and Gordon.<sup>26</sup> They reported a rapid (0.1-s) increase in light absorbance followed by a slow bleaching at 467 nm. They explained these observations by postulating the rapid formation of an inter-halogen oxide intermediate  $\{ClO_2I\}$ , followed by its slow decomposition to  $ClO_2^-$  and  $I_2$ :



Later workers<sup>27</sup> found the electron transfer between  $ClO_2^*$  and  $I^-$  to be fast, implying the chemical impossibility of forming  $\{ClO_2I\}$  in significant concentration. Instead of the formation and slow decomposition of  $\{ClO_2I\}$ , Huie and Neta<sup>27</sup> suggested that the second, slow reaction observed by Fukutomi and Gordon might be the further oxidation of elementary iodine by chlorite ion formed in the fast reduction of  $ClO_2^*$  (reaction C2). It is well-known, however, that the oxidation of iodine to iodate does not take place in the presence of excess iodide ion. Consequently, Huie and Neta's explanation for the slow decrease in absorbance observed by Fukutomi and Gordon cannot be correct. These contradictions in the literature call for a reinvestigation of the reaction.

We repeated Fukutomi and Gordon's experiments in a stopped-flow instrument and found a rapid increase in light absorbance at 468 nm using an excess of iodide ( $[I^-] = 2.45 \times 10^{-2}$  M) over chlorine dioxide ( $[ClO_2^*] = 4.7 \times 10^{-4}$  M) at pH 8.5 (borate buffer). There was, however, no indication of the second phase of the reaction found by Fukutomi and Gordon. In our experiments, the final value of the absorbance was reached in 0.1 s and then remained constant for hours. We suggest that Fukutomi and Gordon's observation is an artifact resulting from their primitive mixing technique, and thus a reliable rate law and rate constants for the  $ClO_2^*-I^-$  reaction are not available. In order to obtain relevant kinetic data for modeling the oscillatory reaction, we found it necessary to study the kinetics of this component process.

We investigated the reaction in acidic medium at low  $[ClO_2^*]$ , the conditions of interest for the oscillatory system. The absorbance change at the isosbestic point of  $I_3^-$  and  $I_2$  (468 nm) was small under these conditions. More accurate results were obtained at 353 nm. Iodide ion was added in excess. Under these conditions, the fast reaction of chlorine dioxide and iodide ion is followed by a slower reaction between the chlorite ion formed and the excess  $I^-$ . The latter reaction is slightly hydrogen ion dependent and results in the production of more iodine. It is a self-inhibited reaction;<sup>28</sup> as we discuss below, its rate decreases with  $[I^-]$  over a wide range of  $[I^-]$ . In Figure 5 we demonstrate that the two reactions can be distinguished by the stopped-flow technique. The

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first, faster part of the curve results from the  $\text{ClO}_2^*-\text{I}^-$  reaction; the second, slow part belongs to the iodide-inhibited  $\text{ClO}_2^*-\text{I}^-$  reaction. The first part was used for the determination of the kinetics of the  $\text{ClO}_2^*-\text{I}^-$  reaction (C2), which was found to be first order with respect to both chlorine dioxide and iodide ion.

$$-\text{d}[\text{ClO}_2^*]/\text{d}t = k_2[\text{ClO}_2^*][\text{I}^-] \quad (\text{R2})$$

Two series of experiments were carried out at pH 2.0 (with  $\text{H}_2\text{SO}_4$  in excess over  $\text{ClO}_2^*$ ) and at pH 5.0 (in 0.2 M acetate buffer). The values of  $k_2$  obtained were  $(6.0 \pm 0.3) \times 10^3$  and  $(5.4 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at pH 2.0 and 5.0, respectively. Thus, the rate depends slightly if at all on pH. We also find the rate to be independent of ionic strength in 0.1–1.0 M  $\text{NaClO}_4$ .

**Chlorite Ion–Iodide Ion Reaction.** Reaction C3 was studied by Kern and Kim,<sup>29</sup> by De Meeus and Sigalla,<sup>30</sup> and by Indelli.<sup>31</sup> We used the rate equation suggested by Kern and Kim.

$$-\text{d}[\text{ClO}_2^-]/\text{d}t = k_{3a}[\text{ClO}_2^-][\text{I}^-][\text{H}^+] + k_{3b}[\text{ClO}_2^-][\text{I}_2]/[\text{I}^-] \quad (\text{R3a})$$

This rate law cannot hold for the entire course of the reaction because as  $[\text{I}^-]$  tends to zero the second term of rate law R3a goes to infinity. Two approaches to this dilemma have been suggested by earlier workers. When  $[\text{I}^-]$  is below a threshold value, Beck and Rábai<sup>13</sup> set the second term in rate eq R3a to zero. A major disadvantage of this treatment is that the rate does not depend continuously on  $[\text{I}^-]$ . Weitz and Epstein<sup>4</sup> add a small number to the denominator of the second term, but with this assumption the rate is finite when all iodide ion has been consumed, which is not chemically realistic. We have adopted the following expression

$$-\text{d}[\text{ClO}_2^-]/\text{d}t = \frac{k_{3a}[\text{ClO}_2^-][\text{I}^-][\text{H}^+] + k_{3b}[\text{ClO}_2^-][\text{I}_2][\text{I}^-]}{u + [\text{I}^-]^2} \quad (\text{R3b})$$

where  $u^{1/2}$  represents the level of  $[\text{I}^-]$  above which the inhibitory effect of iodide ion becomes significant.

The second term in eq R3b goes to zero continuously as  $[\text{I}^-] \rightarrow 0$ . When  $[\text{I}^-]$  is high, the rate equation is the same as Kern and Kim's original equation (R3a). Our revised expression is considerably more stable numerically than those of Kern and Kim or Beck and Rábai.

The second term in eq R3b indicates that the chlorite–iodide reaction is autocatalytic in  $\text{I}_2$  and self-inhibited by  $\text{I}^-$ . Self-inhibition is defined<sup>28</sup> as a decrease in the reaction rate with increasing reactant concentration. In the present system, the autocatalytic character is much less important than the self-inhibitory aspect because during oscillation the relative change in the concentration of the autocatalyst  $\text{I}_2$  is much less than that of the self-inhibitor  $\text{I}^-$ . The effect of self-inhibition on the overall kinetics is very similar to that of autocatalysis, in that both give S-shaped concentration profiles. The two effects can be distinguished by adding some reacted material to the initial mixture; an autocatalytic reaction will be accelerated, while a self-inhibited reaction should be unaffected.

### Modeling the Oscillation

To simulate the behavior of the  $\text{ClO}_2^*-\text{I}_2-\text{MA}$  closed system, we used reactions C1, C2, and C3 with rate equations R1, R2, and R3b. Triiodide ion was considered to be unreactive, and  $[\text{I}^-]$  in the rate equations was modified by taking into account the  $\text{I}_2 + \text{I}^- = \text{I}_3^-$  ( $K = 725 \text{ M}^{-1}$ ) equilibrium. Inclusion of the triiodide equilibrium with a realistic equilibrium constant has no significant effect on the dynamical behavior. We note, however, that the starch indicator employed by most investigators modifies the experimental behavior of the system. The effect of starch can be modeled at least qualitatively by increasing the stability of the unreactive "triiodide" complex.

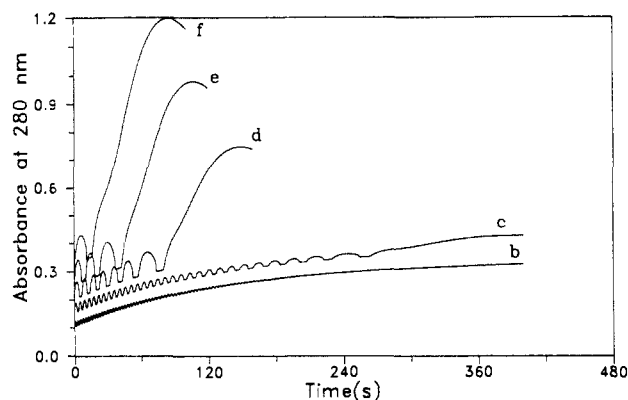


Figure 6. Calculated absorbance–time curves in the  $\text{ClO}_2^*-\text{I}_2-\text{MA}$  reaction. Molar absorbances for  $\text{I}_3^-$ ,  $\text{I}_2$ ,  $\text{ClO}_2^*$ , and iodomalonic acid are 32 000, 100, 88, and  $300 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. Compositions are as in Figure 3.

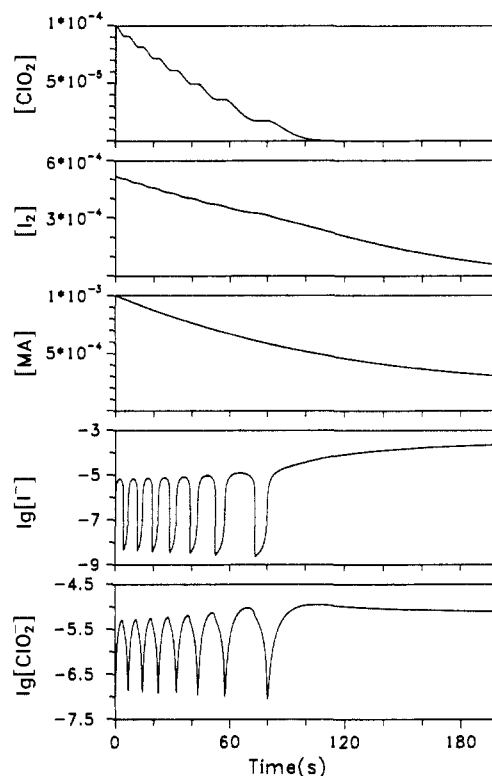


Figure 7. Calculated concentration–time curves:  $[\text{ClO}_2^-]_0 = 1.0 \times 10^{-4}$ ,  $[\text{I}_2]_0 = 5.2 \times 10^{-4}$ ,  $[\text{MA}]_0 = 1.0 \times 10^{-3}$ ,  $[\text{H}_2\text{SO}_4]_0 = 5.0 \times 10^{-3} \text{ M}$ .

With our experimentally determined rate constant for the  $\text{MA}-\text{I}_2$  reaction (C1), the calculated concentration range in which oscillations occur is somewhat narrower than the experimental range. Increasing  $k_{1a}$  from  $5 \times 10^{-3}$  to  $7.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  improves the agreement significantly. During oscillation when  $[\text{ClO}_2^-]$  is high and  $[\text{I}^-]$  low, the oxidation of iodine by chlorite becomes significant and  $\text{HOI}$  can appear as an intermediate. The reaction between  $\text{HOI}$  and  $\text{MA}$  is probably much faster than the  $\text{I}_2-\text{MA}$  reaction. Our neglect of  $\text{HOI}$  in the simple model is partially compensated for by employing a higher rate constant for the iodine–malonic acid reaction. The calculated absorbance curves shown in Figure 6 have initial concentrations corresponding to the experiments pictured in Figure 3. The rate constants used are

$$k_{1a} = 7.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \quad k_{1b} = 5 \times 10^{-5} \text{ M at pH 2}$$

$$k_2 = 6.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{3a} = 4.6 \times 10^2 \text{ M}^{-2} \text{ s}^{-1} \quad k_{3b} = 2.65 \times 10^{-3} \text{ s}^{-1}$$

$$u = 1.0 \times 10^{-14} \text{ M}^2$$

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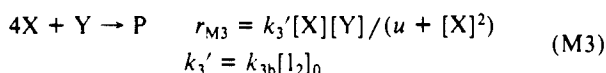
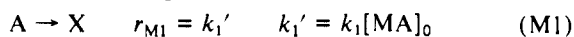
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Both the amplitudes and the number of oscillations are very similar to those found experimentally.

The calculated concentrations of several species are shown in Figure 7. Large-amplitude oscillations are observed in the concentration of the intermediates  $I^-$  and  $ClO_2^-$ . The reactants show relatively slow stepwise decreases in their concentrations. The "steps" are most pronounced in the case of chlorine dioxide, which has the lowest concentration.

The model also simulates successfully the oscillation found in a flow reactor containing  $ClO_2^*$  and  $I^-$  without malonic acid.

As Figure 7 suggests, under a wide range of oscillatory conditions we find that while  $[ClO_2^-]$  and  $[I^-]$  change sharply by several orders of magnitude,  $[ClO_2^*]$ ,  $[I_2]$ , and  $[MA]$  vary much more slowly. We therefore attempted to reduce the above five-variable model to a two-variable system by treating the concentrations of the reactants as constants. The resulting equations are ( $X = I^-$ ,  $Y = ClO_2^-$ )



We have omitted the first term of Kern and Kim's original rate equation because it makes a negligible contribution to the rate under the conditions of interest. On introducing the scaled variables and constants defined in eq 4, we can put the resulting system of differential equations into dimensionless form (eqs 5 and 6):

$$X = \alpha x \quad Y = \beta y \quad t = \gamma \tau \quad \alpha = u^{1/2} \quad (4)$$

$$\beta = uk_2'/k_3' \quad \gamma = 1/k_2' \quad a = k_1'\gamma/\alpha \quad b = \alpha/\beta$$

$$dx/d\tau = a - x - 4xy/(1 + x^2) \quad (5)$$

$$dy/d\tau = b[x - xy/(1 + x^2)] \quad (6)$$

The steady-state solution of eqs 5 and 6 is

$$x_{ss} = a/5 \quad y_{ss} = 1 + x_{ss}^2 \quad (7a)$$

or

$$X_{ss} = k_1'\gamma/5 \quad Y_{ss} = \beta[1 + (X_{ss}/\alpha)^2] \quad (7b)$$

Linear stability analysis shows that this state is unstable if

$$b < 3a/5 - 25/a \quad (8)$$

Since the system has two variables and the concentrations are bounded, the Poincaré–Bendixson theorem<sup>32</sup> guarantees that it will have a periodic solution. Numerical simulations confirm that the solutions tend toward a limit cycle. After back-substitution, eq 8 becomes

$$k_1k_{3b}[MA]_0[I_2]_0 < \frac{3}{5}k_1^2[MA]_0^2 - 25uk_2^2[ClO_2^*]_0^2 \quad (9)$$

This inequality defines the bifurcation surface in the  $[ClO_2^*]$ – $[I_2]$ – $[MA]$  parameter space (Figure 8). We can use expression 9 to determine  $u$  from the value of  $[ClO_2^*]_0$  at which oscillation disappears as the initial chlorine dioxide concentration is varied at fixed  $[I_2]_0$  and  $[MA]_0$ . In the real chemical system, it is not easy to distinguish between the limit cycle and the stable focus (steady state with damped oscillation) because the oscillation disappears in both cases as a result of the consumption of the reactants. Our calculations show that near the bifurcation surface trajectories that approach the limit cycle or the stable point can be very similar during the transient phase. The only guide is that in most cases the limit-cycle oscillations disappear with increasing amplitude. The stable focus will always be approached by damped oscillations.

The experimental range of oscillation in a closed system as the initial concentrations of chlorine dioxide, iodine, and malonic acid

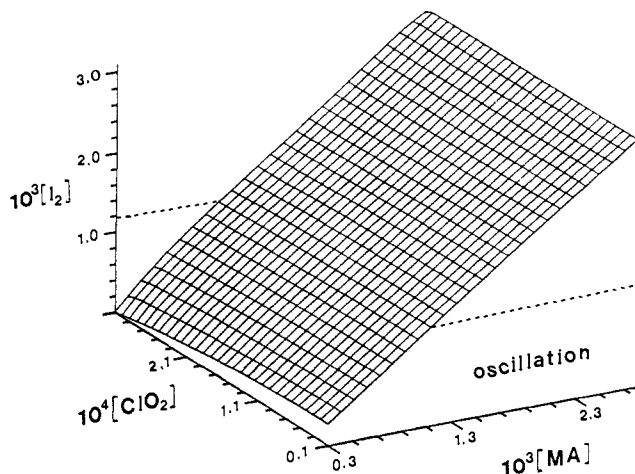


Figure 8. Bifurcation surface between oscillatory and nonoscillatory behavior calculated with the two-variable model. Dashed line indicates the solubility limit of iodine. The oscillatory compositions lie below the surface.

are varied is well described by eq 9. The two-variable model implies that there is no lower limit on  $[ClO_2^*]$  for oscillation. Clearly, when the chlorine dioxide consumed in one period is comparable to its initial concentration, oscillation must cease. The two-variable model, which takes  $[ClO_2^*]$  to be constant, is unable to take into account this limitation, but, as seen in Figure 6, the more detailed five-variable model does show the cessation of oscillation as the reactant is consumed. The range of validity of the two-variable model should be broader in simulating the open-system behavior because the inflow replenishes the reactants consumed in each period of oscillation.

## Discussion

A model with an inhibitory process similar to that of eq R3b or M3 has been suggested by Degn and Harrison<sup>33</sup> to describe oscillations in certain biochemical systems. The properties of that model have been investigated by Velarde and co-workers,<sup>34,35</sup> who demonstrated the existence both of limit cycles in a homogeneous system and of dissipative structures in a spatially inhomogeneous system.

The two-variable simplified model we have proposed obviously has limitations, particularly in closed systems where reactant consumption must ultimately become significant. Nonetheless, we have shown that the model describes the dynamics of the system remarkably well. In view of the considerable interest in the Turing structures recently found in the chlorite–iodide–malonic acid system,<sup>10</sup> the availability of such a simple model on which detailed mathematical analysis is feasible makes the chlorine dioxide–iodine–malonic acid reaction an attractive one for further investigation.

The studies presented here have resulted in a better description of the component processes of the chlorine dioxide–iodine–malonic acid system. The description we have presented is perhaps better characterized as an empirical rate law model than as a full mechanism for this complex reaction. We plan further studies to develop a mechanism consisting of elementary steps that will provide a coherent description of the variety of phenomena found in the present system and in the related chlorite–iodide reaction.<sup>36</sup>

Finally, we point out that while the chlorite–iodide reaction is autocatalytic, the key to the behavior of the system studied here appears to be the self-inhibition. Self-inhibition (or substrate inhibition) is a common feature of biochemical reactions, but it has received relatively little attention in the chemical literature. The incorrect notion that autocatalysis is a necessary condition

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for oscillation has even found its way into widely used textbooks of physical chemistry.<sup>37</sup> It is important to bear in mind that self-inhibition provides another form of feedback that can lead to chemical oscillation. While this is the first self-inhibitory chemical oscillator of which we are aware, it is likely that there

are many more oscillatory reactions based on self-inhibition that are waiting to be discovered.

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## Role of Ion–Neutral Complexes during Acid-Catalyzed Dehydration of Ethanol in the Gas Phase

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**Abstract:** Acid-catalyzed dehydration of ethanol in the gas phase has been studied both theoretically and experimentally. Molecular orbital calculations have been done at the MP3/6-31G\*\*//6-31G\* level with correction of the zero-point vibrational energy. Protonated ethanol, **1** is predicted to isomerize easily into the  $C_2H_4 \cdots H \cdots OH_2^+$  complex, **2** (activation energy 120 kJ/mol). This result is in agreement with the observation of a near statistical hydrogen exchange preceding the dehydration reaction  $1 \rightarrow C_2H_4 + H_3O^+$ . In the case of the water-solvated ion  $C_2H_5OH_2 \cdots OH_2^+$ , **5**, isomerization into a proton-bound complex  $C_2H_4 \cdots H_3O_2^+$ , **6**, needs a larger amount of energy (ca. 180 kJ/mol). Again the calculations agree with experiments: the important activation energy for the process  $5 \rightarrow 6$  prevents hydrogen exchanges and ethene elimination. Extension of these conclusions to higher systems is discussed.

1,2 elimination reactions are of fundamental interest in organic chemistry and are ubiquitous processes in gas-phase chemistry of cationic or anionic species. For such reactions, some mechanistic proposals presently encountered in the literature involve ion-neutral complexes, i.e., species in which noncovalent interactions retain close together two entities able eventually to react unimolecularly or bimolecularly, as key intermediates.<sup>1–3</sup> In the case of a protonated species, a suggested dissociation mechanism implies formation of an elusive proton-bound complex as summarized in Scheme 1.

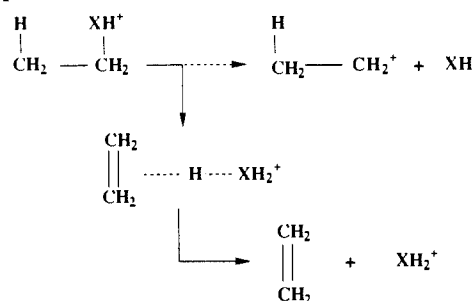
Starting from  $CH_3CH_2XH^+$ , the direct C–X bond elongation leads to the products  $C_2H_5^+$  and XH. During this process, interaction between these two products may give rise to a proton-bound intermediate which, in turn, decomposes into  $C_2H_4 + XH_2^+$ .

Dehydration of protonated alcohols is a common type of elimination reaction whose description may enter into this frame. The purpose of the present work is to test the validity of Scheme 1 in providing a reasonable view of the potential energy surface associated with dehydration of protonated alcohols in the gas phase. Therefore, investigations on the prototype systems  $C_2H_5OH_2^+$  ( $C_2H_5OH_2^+$ ,  $H_2O$  and  $C_2H_5OH_2^+$ ,  $C_2H_5OH$ ) have been done by means of molecular orbital calculations and comparison has been made with mass spectrometry experiments.

### I. Dehydration of Protonated Ethanol

In the gas-phase  $C_2H_5OH_2^+$ , **1**, may be produced by protonation of ethanol under chemical ionization conditions<sup>4–10,19–21,31</sup> or by

Scheme 1



condensation reaction between  $C_2H_5^+$  ions (coming, for example, from  $C_2H_5Br$ ) and a water molecule.<sup>8</sup>

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