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### Appendix: The Heat of Formation of HCO

Experimental values for  $\Delta H_f^\circ[\text{HCO}]$  come from four different sources: photoionization studies, photodecomposition studies, HCO self-recombination studies, and iodine-formaldehyde studies. The most direct photoionization experiments are those of Warneck,<sup>37</sup> who measured the threshold for  $\text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}^+ + \text{e}^-$  at room temperature. When corrected<sup>38</sup> to 0 K, this threshold, together with JANAF values<sup>39</sup> of heats of formation of H,  $\text{H}^+$ ,  $\text{e}^-$  and  $\text{H}_2\text{CO}$ , gives  $\Delta H_f^\circ[\text{HCO}] = 12.1 \pm 1.8$  kcal/mol. The best photodecomposition studies<sup>40</sup> measured the onset of HCO production as a function of photon energy in the laser-induced decomposition of  $\text{H}_2\text{CO}$  at room temperature. When corrected to 0 K either empirically<sup>41</sup> or theoretically,<sup>38</sup> the resulting value

of  $\Delta H_f^\circ[\text{HCO}]$  is  $9.7 \pm 1.2$  kcal/mol. HCO self-recombination studies are the basis for the JANAF value<sup>39</sup> for  $\Delta H_f^\circ[\text{HCO}]$  of  $10.3 \pm 2.1$  kcal/mol.

The last measurement<sup>42</sup> involves an equilibrium study of  $\text{I} + \text{H}_2\text{CO} \rightleftharpoons \text{HI} + \text{HCO}$  in which the activation energies for the forward and reverse directions are separately measured. The difference of these energies, corrected to 0 K, together with the known<sup>39</sup> thermochemistry of I and HI gives  $\Delta H_f^\circ[\text{HCO}]$ . In the measurements, the forward activation energy is measured to within  $\pm 0.2$  kcal/mol. However, the reverse reaction activation energy is not directly measured. Rather, the difference of that activation energy from one for a secondary reaction is directly measured with an uncertainty of about  $\pm 0.9$  kcal/mol. This secondary reaction activation energy is estimated to be between 0 and 1 kcal/mol, for an uncertainty of  $\pm 0.5$  kcal/mol. The final value of  $\Delta H_f^\circ[\text{HCO}]$  is  $9.9 \pm 1.6$  kcal/mol where the final uncertainty is the sum of those for the individual measurements.

The four measured values of  $12.1 \pm 1.8$ ,  $9.7 \pm 1.2$ ,  $10.3 \pm 2.1$ , and  $9.9 \pm 1.6$  kcal/mol have an overlapping range of about 2 kcal/mol centered at about 10.3 kcal/mol, suggesting a consensus value of  $10.3 \pm 1.0$  kcal/mol.

**Registry No.** HCO, 2597-44-6; H, 12385-13-6; CO, 630-08-0;  $\text{D}_2$ , 7782-39-0.

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## New Dynamic Behaviors in a Closed Iodide-Catalyzed Bromate Oscillator. Experiments and Their Mechanistic Interpretation

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When iodide ion is initially present in a closed, uncatalyzed bromate oscillator with 4-[2-(methylamino)propyl]phenol as the organic substrate, a dramatically higher number of oscillations (at most over 100) can be generated than is observable in the absence of iodide ion (3–6 oscillations). The mixing order of reactant solutions was found to have a major influence on the number of oscillations observed. This can be explained by the recently found "clock-type behavior" of the bromate-iodide reaction. The iodide-catalyzed oscillations are explained in terms of a recycling of iodine between oxidation states +I and -I where reactive iodine(+I) intermediates react rapidly with the organic substrate and thus prevent further effective oxidation of iodine to iodate by bromate. Bromide ions are produced by subsequent reactions, and control of oscillations is interpreted by analogy to the Field-Körös-Noyes theory, with bromide ion as the control intermediate. Similarities to the iodide-bromate reaction performed under batch and CSTR conditions are discussed. We found the first example of a bistability between an oscillatory and a nonoscillatory state in a closed system.

### Introduction

Bromate oscillators<sup>1,2</sup> are homogeneous oscillatory chemical reactions in which an organic substrate is brominated and oxidized by bromate ion in aqueous acidic solutions. They can be divided into two major groups. The first consists of the catalyzed or "classical"<sup>1</sup> bromate oscillators, where a metal ion serves as a catalyst. The other main group includes the so-called uncatalyzed systems where no metal ion catalyst is present.<sup>3,4</sup> Basic mechanisms have been established for both classes: the Field-Körös-Noyes (FKN)<sup>5</sup> mechanism for the catalyzed case and the Orbán-Körös-Noyes (OKN)<sup>6</sup> mechanism for uncatalyzed systems; the OKN mechanism is a minor modification of the FKN mechanism.

The important feature in both mechanisms is that bromide ion has a basic function as a control intermediate switching the system between an oxidized and a reduced state, corresponding to a low and high bromide ion concentration, respectively. Model calculations<sup>7,8</sup> show that main features appear to be reasonably well

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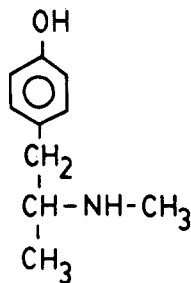


Figure 1. The organic substrate 4-[2-(methylamino)propyl]phenol.

understood, although mechanistic details, especially for the organic parts of the various systems, still need further investigation.<sup>9</sup>

When bromination is slow, or not possible, bromine ( $\text{Br}_2$ ) builds up. In such cases control of oscillations is still due to bromide ion, but the source of bromide ion is the hydrolysis of dissolved bromine.<sup>10</sup> Bromine hydrolysis control of oscillations is possible in both catalyzed and uncatalyzed systems.<sup>8,10</sup>

Uncatalyzed bromate oscillators in closed systems exhibit only a few oscillations and a high damping factor.<sup>3,4</sup> Recently, Varga et al.<sup>11</sup> observed that, for certain types of organic substrates, initially added iodide ion—in a rather narrow concentration range—can increase the number of oscillations considerably and alter the length and character of the preoscillatory period. The effect is similar to earlier reported effects of iodide ion on the cerium ion catalyzed malonic acid oscillator.<sup>12,13</sup>

Ruoff<sup>14</sup> showed that when solutions of bromide ion or iodide ion are pumped into a catalyzed bromate oscillator which is in an oxidized steady state, relaxation oscillations can be induced. These oscillations are explained in terms of the excitability property of the oxidized steady state, by analogy with previous reported excitabilities and induced oscillations of the reduced steady state.<sup>15–18</sup>

The present study was undertaken to see whether iodide ion promoted oscillations in uncatalyzed systems can be understood in terms of the excitability property of the oxidized steady state. We find that for iodide ion induced oscillations the oxidized steady state is locally stable. An excitation does not lead to a return to the (oxidized) state but leads to an oscillatory state. On the other hand, by addition of silver ion beyond a certain threshold concentration to the oscillatory state, the system switches back to the nonoscillatory oxidized state. This is the first example of a bistability between an oscillatory and a nonoscillatory state observed in a closed chemical system. We believe that this behavior observed under batch conditions is closely related to similar observations by Alamgir et al.<sup>19</sup> in the bromate–iodide reaction in CSTR mode.

We also show that initial mixing order has an enormous influence on the period length and the size of the oscillatory region. Finally, possible mechanistic interpretations of our observations are discussed.

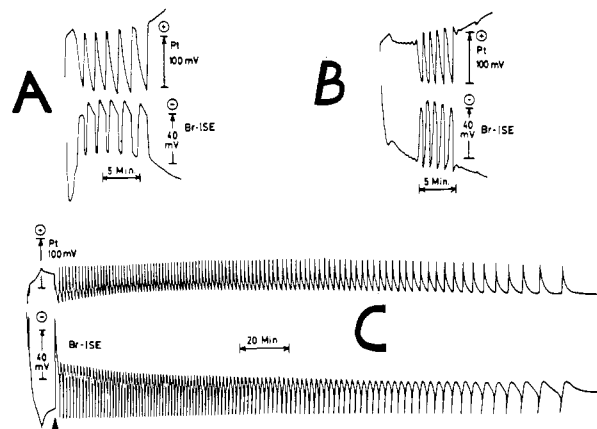


Figure 2. (A) Uncatalyzed bromate oscillator with the following initial composition:  $[\text{HMP}] = 0.03 \text{ M}$ ,  $[\text{KBrO}_3] = 0.05 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ . (B) Same initial concentrations as in (A), but in addition also containing  $4 \times 10^{-3} \text{ M KI}$ . Mixing of reactant solutions was performed in the following order: 27.5 mL of  $\text{H}_2\text{O}$ , 5 mL of 10 M  $\text{H}_2\text{SO}_4$ , 10 mL of 0.25 M  $\text{KBrO}_3$ , 2 mL of 0.1 M  $\text{KI}$ , and finally 7.5 mL of 0.2 M  $\text{HMP}$ . (C) Same initial reagents as in (B), but mixing of initial reagent solutions was performed in the order  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HMP}$ ,  $\text{KI}$ ,  $\text{KBrO}_3$ . Arrow at the left lower part of the figure indicates the addition of one drop of a 0.1 M  $\text{KI}$  solution.

### Experimental Section

The experiments were performed in a commercial polarographic cell (Metrohm, Switzerland) at a constant temperature of  $25^\circ\text{C}$  ( $\pm 0.1^\circ\text{C}$ ) and with magnetic stirring. The oscillations were followed by means of a platinum electrode and a bromide ion selective electrode (Br-ISE, Metrohm) against a double-junction  $\text{Ag/AgCl}$  reference electrode (sleeve type, Metrohm) with 1 M sulfuric acid (which was also the reaction medium) as the outer electrolyte. The oscillations were recorded on a conventional two-channel  $x-t$  recorder (Kipp & Zonen, Holland).

We also tested an iodide ion selective electrode (I-ISE, Radelkies, Hungary) but found no difference in our experiments compared with the Br-ISE. The reason for this is that in our system the I-ISE responds exclusively to bromide ion because iodide ion is present at a much lower concentration level than bromide ion (see Discussion section).

All chemicals, except the organic substrate, were of commercial analytical quality from which stock solutions were prepared. The organic substrate was the sulfate salt of 4-[2-(methylamino)propyl]phenol (denoted as in an earlier publication<sup>11</sup> as HMP; Figure 1) with a purity greater than 99%.

The total reaction volume was 50 mL, and oscillations were started by mixing stock solutions in the following order: 27.5 mL (25.5 mL) of  $\text{H}_2\text{O}$ , 5.0 mL of 10 M  $\text{H}_2\text{SO}_4$ , 7.5 mL of 0.2 M  $\text{HMP}$  (2.0 mL of 0.1 M  $\text{KI}$ ), 10 mL of 0.25 M  $\text{KBrO}_3$ . If the  $\text{KI}$  is omitted, we have a simple uncatalyzed oscillator. We also used the mixing order  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KI}$ ,  $\text{KBrO}_3$ ,  $\text{HMP}$ , where the  $\text{HMP}$  stock solution is added at the end.

The total oxidizing power (TOP) expressed as molarity in bromate was determined by the following procedure. Aliquots (3 mL) were withdrawn from the reaction mixture and added to an Erlenmeyer flask containing 20 mL water, 5 mL of 2 M  $\text{HCl}$ , and solid anhydrous  $\text{Na}_2\text{CO}_3$ . The sodium carbonate was added in order to remove the air from the titration vessel and to avoid possible oxygen interferences. Then solid  $\text{KI}$  was added in excess, and the liberated iodine was titrated with a 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch for the detection of the end point. The amount of bromate was calculated according to the stoichiometry of reaction R1.

### Results

**Influence of Initial Mixing Procedures.** Different mixing orders of the initial reagents for iodide ion promoted uncatalyzed bromate oscillators have a dramatic influence on the number of oscillations. Figure 2A shows the behavior of an uncatalyzed HMP oscillator

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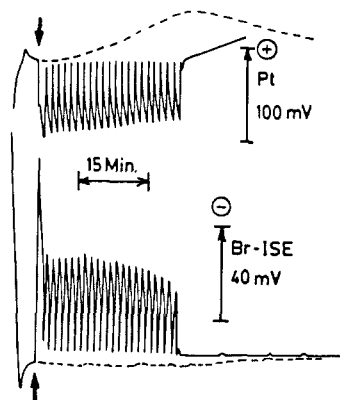
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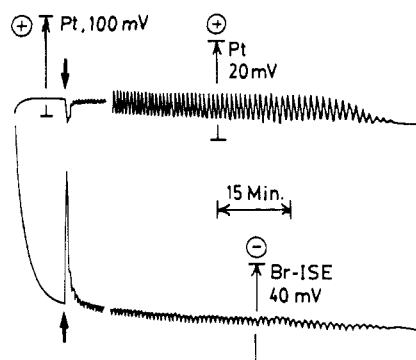
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**Figure 3.** Iodide-catalyzed bromate oscillator with following initial concentrations:  $[H_2SO_4] = 1.0$  M,  $[HMP] = 0.03$  M,  $[KBrO_3] = 0.05$  M,  $[KI] = 3 \times 10^{-3}$  M with mixing procedure of Figure 2C. Arrows indicate the addition of one drop of a 0.1 M KI solution. The dashed lines show the nonoscillatory potential response of an identical system but with the single drop KI perturbation omitted.

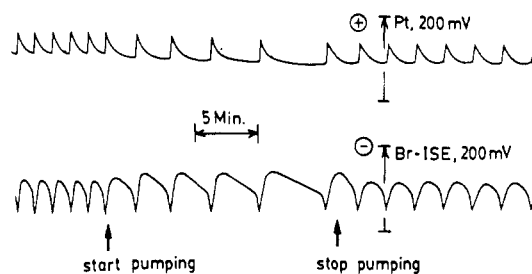


**Figure 4.** Small-amplitude and high-frequency oscillations of an iodide-catalyzed bromate oscillator with the following initial concentrations:  $[H_2SO_4] = 1.0$  M,  $[HMP] = 0.03$  M,  $[KBrO_3] = 0.05$  M,  $[KI] = 5 \times 10^{-3}$  M with initial mixing procedure of Figure 2C. The arrows in the beginning indicate addition of one drop of a 0.1 M KI solution ( $6 \times 10^{-5}$  M).

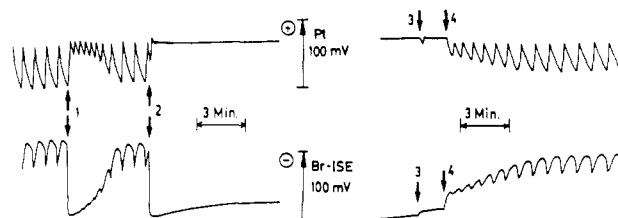
with 0.03 M HMP and 0.05 M  $KBrO_3$  in 1 M  $H_2SO_4$ . Only a few oscillations are observed. The situation is almost unchanged (Figure 2B) when—for the same initial HMP and  $KBrO_3$  concentrations— $4 \times 10^{-3}$  M KI is added by using the following initial mixing procedure:  $H_2O$ ,  $H_2SO_4$ , KI,  $KBrO_3$ , and finally HMP. However, if mixing of the stock solutions is done in the order  $H_2O$ ,  $H_2SO_4$ , HMP, KI,  $KBrO_3$ , then the number of oscillations increases drastically as shown in Figure 2C. In this case over 100 oscillations are observed! Such a large number of oscillations have never before been observed in iodide ion promoted uncatalyzed or ordinary uncatalyzed systems!

**Effect of Iodide, Bromide, and Silver Ions.** Another interesting observation, also shown in Figure 2C, is that oscillations can be initiated by adding a relatively small amount of KI to the system. The arrow in the left lower part of Figure 2C indicates the addition of one drop of a 0.1 M KI solution. Depending slightly upon the drop size, this perturbation is in the order of 1–2% of the total initially added KI. If the iodide perturbation is not applied, oscillations either may appear later with a gradual increase in amplitude or may be completely absent as shown in Figure 3. The iodide perturbation was applied to determine whether oscillations could be generated. However, no oscillations could be induced by iodide ion after oscillations of a purely uncatalyzed system (without any initial iodide) had finished.

The concentration range of initially added iodide ion which can generate oscillations (after the slight iodide perturbation) was found to be quite narrow, i.e., between  $3 \times 10^{-3}$  and  $5 \times 10^{-3}$  M KI. This is about the same range as previously found by Varga et al.<sup>11</sup> At the high end of the initial KI concentration range, the oscillations are markedly different from those when the initial KI concentration is low. At high initial KI concentrations we observe



**Figure 5.** Effect of pumping a  $10^{-3}$  M KI solution into an oscillatory iodide-catalyzed bromate oscillator identical with the system of Figure 2C using a peristaltic pump (ISCO WIZ, U.S.A.). Pumping rate: 40 mL/h.



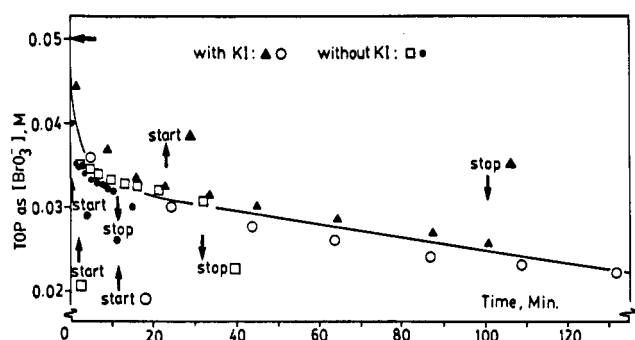
**Figure 6.** Temporary bistability between an oscillating and a nonoscillating state of an iodide-catalyzed HMP oscillator. The system is identical with that of Figure 2C, and transitions were performed a few minutes after oscillations have been initiated: (1) Addition of five drops of a  $10^{-2}$  M  $AgNO_3$  solution ( $3.0 \times 10^{-5}$  M). After a few minutes the oscillations reappear. (2) Addition of six drops of a  $10^{-2}$  M  $AgNO_3$  solution ( $3.6 \times 10^{-5}$  M). The system does not return to the oscillatory state but remains in the nonoscillatory (oxidized) steady state. (3) 36 min after perturbation 2, one drop of a  $10^{-2}$  M KI is added ( $6.0 \times 10^{-6}$  M). The system remains in the oxidized state and shows that the state is locally stable. (4) Two drops of a  $10^{-2}$  M KI is added ( $1.2 \times 10^{-5}$  M). The system returns to the oscillatory state.

high-frequency and small-amplitude oscillations. Typical behavior is shown in Figure 4.

The same effects are found if bromide ion is used as the *perturbing* agent instead of iodide ion. For example, oscillations can also be initiated by adding a single drop of a 0.1 M KBr solution into the system instead of using KI. Pumping diluted solutions of KBr or KI into an iodide promoted uncatalyzed system always causes an increase in period length (Figure 5). This effect is somewhat unexpected to us, because we thought that both iodide and bromide ion would act as a trigger, i.e., decrease period lengths in the same way as recently observed<sup>14</sup> for an oxidized nonoscillating excitable steady state.

When silver ion is added to the oscillatory state of the iodide ion promoted system, we observe first high-frequency “silver ion induced oscillations” where the Br-ISE shows an almost monotonic behavior (Figure 6). This particular behavior (observed in both catalyzed and uncatalyzed systems) is now well understood,<sup>17,18</sup> because the Br-ISE responds to the monotonic excess silver ion concentration. When the added silver ion exceeds a certain threshold value, the system remains in the oxidized state and does not return to the original oscillatory state. The system remains in the (nonoscillatory) oxidized state as long as enough bromate is present to maintain this state. If this oxidized nonoscillatory state is now perturbed by iodide (or bromide ion; we show the results with iodide ion), the system switches back to the oscillatory state when a certain concentration threshold of iodide (or bromide) is exceeded. For the system of Figure 6, transitions between the oscillatory and the nonoscillatory state can be induced for about 1 h after oscillations have been initiated. This observation is the first example of a bistability between an oscillatory and a nonoscillatory state in a *closed* system. It is the second example of a (temporary) bistability in a closed chemical system.<sup>20</sup>

**Effect of Gas Bubbling.** When oxygen, air, or nitrogen is bubbled through a system (identical with the one of Figure 2C) during its oscillatory period, no influence of these gases is observed



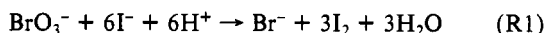
**Figure 7.** The total oxidizing power (TOP) expressed as  $[\text{BrO}_3^-]$  as a function of time. The figure shows two parallel runs of respectively an uncatalyzed system ( $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ ,  $[\text{HMP}] = 0.03 \text{ M}$ ,  $[\text{KBrO}_3] = 0.05 \text{ M}$ ) and an iodide-catalyzed system (with  $4.0 \times 10^{-3} \text{ M KI}$ ). Arrows up combined with a particular symbol indicate the start of oscillations. Arrows down combined with the symbol indicate stop of oscillations. Oscillations of the iodide-catalyzed system which is represented by the open circles stopped about 4 h after mixing of initial reagent solutions.

on the oscillations. However, when gas bubbling is started during the initial mixing of the reagents, no oscillations could be generated by applying the KI perturbation.

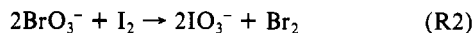
**Bromate Consumption.** We determined the total oxidizing power (TOP) expressed as  $[\text{BrO}_3^-]$  both for simple uncatalyzed systems and for systems containing initial iodide ion. Bromate consumption was almost the same in both systems (Figure 7).

## Discussion

**Explanation of Effects of Initial Mixing Orders and Gas Bubbling.** When bromate ion is in excess, the oxidation of iodide in a closed system recently was found to proceed in a "clock-type behavior".<sup>21</sup> In the first stage of the process, iodide ion is oxidized by bromate to iodine:



The second process (R2) is the rapid oxidation of iodine by bromate. However, this reaction does not start until process R1



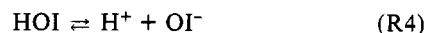
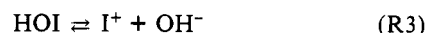
is complete. It appears that the different dynamic behaviors observed in Figure 2B,C can be explained by the consecutive character of reactions R1 and R2.

When mixing of the initial reagents is performed in the order  $\text{H}_2\text{SO}_4$ , KI,  $\text{KBrO}_3$ , HMP, the iodine formed by process R1 is oxidized by reaction R2 to higher oxidation states and iodide before finally HMP is added. This we have observed by the decolorization of the solution due to  $\text{I}_2$  oxidation, which was complete before we were able to add HMP. Under such conditions, only minor amounts of the initially available iodine will be available to react with the organic substrate.

However, in the case when bromate rather than HMP is added last, reactive intermediates which are formed during the oxidation of iodide by bromate are now able to react with the organic substrate. Preliminary experiments with HMP and HME<sup>11</sup> show that  $5 \times 10^{-3} \text{ M I}_2$  appears not to react with the organic substrate (no decolorization of the solution observed even after 24 h), while the same amount of HOI generated in situ reacts rapidly with the organic substrate. (HOI is followed by the redox potential of a platinum electrode.) We therefore believe that HOI and possibly also the  $\text{I}^+$  ion are important intermediates in this respect.

HOI has amphoteric properties with a dominating basicity and forms the  $\text{I}^+$  ion, which—besides HOI—is known to be a strong iodination agent especially in acidic media.<sup>22a</sup> In aqueous solutions  $\text{I}^+$  should probably be written as  $\text{I}^+\cdot\text{H}_2\text{O}$  which is the protonated

form of HOI.<sup>22b</sup> The effectiveness as iodination agents decreases rapidly in the order  $\text{I}^+ > \text{HOI} > \text{I}_2$ .<sup>23</sup> Equilibrium constants of dissociation reactions R3 and R4 (at  $25^\circ\text{C}$ ) are  $3.2 \times 10^{-10}$  and  $4.5 \times 10^{-13}$ , respectively.<sup>24</sup>



Generally, iodine (in the form of  $\text{I}^+$  ( $\text{IOH}_2^+$ ), HOI, but also by the slower  $\text{I}_2$ ) attacks aromatic compounds only at the (aromatic) core and almost exclusively by an ionic substitution reaction. The direct incorporation of iodine into an aliphatic side chain is seldomly observed and probably involves radical processes.<sup>25,26</sup>

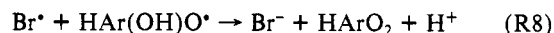
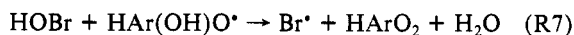
Besides an iodination agent, HOI is also a strong oxidizing compound.<sup>27</sup> In this case, the methylene group in the side chain can be oxidized,<sup>28</sup> besides the aromatic core oxidation to quinones.<sup>4,11</sup>

The iodination or oxidation reactions of the iodine intermediates with the organic substrate should be faster than the HOI oxidation by bromate (reaction R5) in order to prevent further rapid ox-



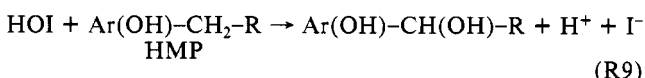
dation to iodate.<sup>21</sup> Citri and Epstein<sup>29</sup> proposed a rate constant of reaction R5 in the order of  $8 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$ , which is the rate-determining step of the HOI oxidation to iodate in the iodide-bromate reaction.<sup>21,29</sup>

In purely uncatalyzed bromate oscillators,<sup>3,4</sup> bromide ion, the control intermediate, is regenerated by organic radicals.<sup>6</sup>

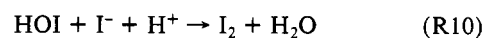


In the case when the iodide ion is initially present, we think that the HOI/ $\text{I}^+$  intermediate are now—indirectly—the source of bromide ion by reactions with oxybromine species, probably by reactions with HOBr.

Preliminary results by Varga et al.<sup>11</sup> with different alkylated phenols indicate that the aliphatic side chain is the reactive site of the possible HOI/ $\text{I}^+$  attack. It was assumed that this is an iodination followed by a hydrolysis,<sup>11</sup> but it appears that also HOI oxidation of the side chain could be an important process, and oscillations in Figure 2C might be explained by the following bromide ion regenerating processes.



Iodide ion produced by reaction R9 will be immediately consumed in reaction R10. This is an extremely fast process with



the equilibrium far on the  $\text{I}_2$  side,<sup>30</sup> which keeps the iodide ion concentration at a very low level. This is the reason why the I-ISE does not respond to iodide ion but to bromide ion. The maximum permissible concentration ratio for an I-ISE between bromide and

(23) Soper, F. G.; Smith, G. F. *J. Chem. Soc.* **1927**, 2757.

(24) Roedig, A. In *Methoden der Organischen Chemie (Houben-Weyl)*, Vierte Auflage, Band V/4, Halogenverbindungen; Müller, E., Ed.; Thieme: Stuttgart, 1960; p 524, footnote 1.

(25) Offe, H. A. *Ber. Dtsch. Chem. Ges.* **1938**, 71, 1837.

(26) Reference 24, p 558.

(27) *Gmelins Handbuch der Anorganischen Chemie*, Achte Auflage, Jod, System-Number 8; Verlag-Chemie: Berlin, 1933; p 450 ff.

(28) Weickmann, A.; Zeller, K.-P. In *Methoden der Organischen Chemie (Houben-Weyl)*, Vierte Auflage, Band IV/1a, Oxidation, Teil I; Kropf, H., Ed.; Thieme: Stuttgart, 1981; p 495 ff.

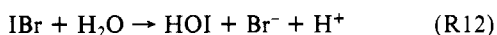
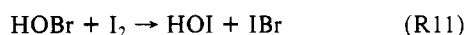
(29) Citri, O.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, 108, 357.

(30) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, 84, 1355.

(21) Simoyi, R. H.; Masvikieni, P.; Sikosana, A. *J. Phys. Chem.* **1986**, 90, 4126.

(22) (a) Berliner, E. *J. Am. Chem. Soc.* **1950**, 72, 4003. (b) Bard, A. J.; Parsons, R.; Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985; p 86 f and references therein.

iodide ion is about  $5 \times 10^3$ . When this ratio is exceeded, the I-ISE begins to respond to bromide ion.<sup>31</sup> Numerical data provided by Citri and Epstein<sup>29</sup> indicate that this concentration ratio is exceeded by several orders of magnitude, and also these authors conclude that the I-ISE's potential is due to bromide and not due to iodide ion. The iodine formed is then further oxidized by HOBr to bromine and HOI:

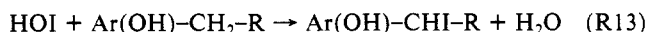


The rate constants of (R11) and (R12) are not known, but Citri and Epstein<sup>29</sup> have provided numerical estimates in a recent model of the iodide-bromate reaction.<sup>19</sup>

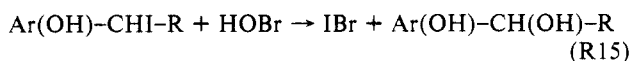
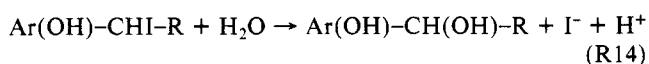
The HOI formed will then again be able to oxidize the organic substrate. This "recycling" of HOI prevents further effective oxidation of HOI to iodate, and we believe that such a "recycling process" which keeps most iodine in an oxidation state +I (either temporarily organically bounded or/and as free HOI) is responsible for the extreme number of oscillations observed in Figure 2C.

Due to the "clock-type behavior" of reactions R1 and R2, we can also show why oscillations are not observed when gas (air,  $\text{N}_2$ ,  $\text{O}_2$ ) is bubbled into the system during mixing but no effect of gas bubbling is observed after oscillations have started. Our explanation of this effect is that when gas bubbling starts from the beginning, the initially available iodide ion is first, according to process R1, oxidized to  $\text{I}_2$  until further oxidation (process R2) can proceed. During this stage, gas bubbling will remove<sup>32</sup> the entire iodine content as  $\text{I}_2$  and the system remains in a nonoscillatory state. When  $\text{N}_2$ ,  $\text{O}_2$ , or air bubbling is started after the first oscillations have appeared,  $\text{I}_2$  will be at a much lower concentration level, such that gas bubbling apparently has no effect.

Although iodination of HMP by HOI or  $\text{H}_2\text{OI}^+$  is normally expected to occur at the aromatic core, rapid iodination could also be possible at the aliphatic side chain:<sup>11</sup>



Once the iodo-organic compound has been formed, it may be subject to several reactions. It could further react by hydrolysis (R14), which primarily occurs in strongly acidic media<sup>33</sup> and where the iodide ion formed is rapidly oxidized to HOI and bromide ion (R10-R12), or the iodo-organic could react directly with HOBr by process R15, where IBr reacts further according to process R12.



In fact, it appears that the aliphatic side chain is essential: no iodine-promoted oscillations are observed in systems which contain aromatics without a side chain, i.e., 1,2,3-trihydroxybenzene or 3,4,5-trihydroxybenzoic acid.

**Comparison with the Iodide-Bromate Reaction in a CSTR.** Alamgir et al.<sup>19</sup> studied the iodide-bromate reaction in a CSTR, and recently Citri and Epstein<sup>29</sup> proposed a detailed mechanism.

The organic substrate in our system appears to have a similar function as the flow in the Alamgir et al.<sup>19</sup> study, i.e., the repeated

supply of iodide, which in our case is achieved by the "recycling reactions" R9, R13, or R14.

The study of Alamgir et al.<sup>19</sup> described the first example of a bistability between a nonoscillatory and an oscillatory state. This, we believe, is closely connected to our observation of a temporary bistability between an oscillating and a nonoscillating state in a closed system (Figure 6).

The model of Citri and Epstein<sup>29</sup> shows good agreement between experiments and simulations, and it also successfully describes the transition between the oscillatory and a nonoscillatory state in a CSTR. While the Citri and Epstein model does not involve any radical reactions, we are presently not able to exclude possible radical reactions of iodine with the organic substrate. We will return to this question in a further experimental study on isolated component processes of this system.

The dashed lines in Figure 3 show that oscillations may be completely absent when the initial iodide or bromide perturbations are not used. This indicates that there is a locally stable, nonoscillatory steady state, which is surrounded by a limit cycle. During the time when the locally stable steady state coexists with the limit cycle, it is possible to induce transitions between these two states. This makes the connection to our observation of a bistability between an oscillatory and a nonoscillatory state (Figure 6).

However, there is a difference between the iodide-bromate bistability observed in a CSTR<sup>19,29</sup> and the bistability in our Figure 6. The experiments by Epstein and co-workers<sup>19,29</sup> show that the nonoscillating state has a lower platinum potential than the oscillatory state. However, our experiments (Figure 6) show transitions between states which both exhibit a *high* platinum potential. If the Citri and Epstein model of the iodide-bromate reaction can be applied to our observed bistability, then Figure 6 would imply a *horizontal* transition in Figure 3a of ref 29 between the oscillatory state and the (to the oscillatory state) *connected* nonoscillatory state. We will return to this question in a further simulation study.

When solutions of iodide or bromide ions are pumped into an oscillatory system of an iodide-catalyzed HMP-bromate oscillator, we observe an increase in period length. (Figure 5 shows the results with bromide ions.) The observation of an increased period length implies that the oscillations are not the result of the excitability property of the oxidized steady state, as recently proposed for another system.<sup>14</sup> The difference from ref 14 is that the oxidized steady state in the present study is not subject to a simple excitation with the return to the oxidized steady state but stays after the excitation in an oscillatory state.

**Bromate Consumption.** Figure 7 shows that during the first 5 min about 30% of the initially available bromate ion is reduced, and no significant difference in bromate consumption is observed whether or not iodide is present. It appears that bromate reacts directly with the organic substrate. Further study has to show the details of this rapid bromate consumption.

## Concluding Remarks

There are presently several possibilities to explain the catalytic effect of iodine in bromate oscillators. Our results so far indicate that very reactive intermediates like HOI or  $\text{IOH}_2^+$  are an indirect but effective source of the bromide ion, but we presently do not know the precise way in which these reactive iodine intermediates react with our organic substrate or with the inorganic oxybromine species. Further experimental work and subsequent simulation calculations are being considered.

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**Registry No.** HMP, 370-14-9;  $\text{BrO}_3^-$ , 15541-45-4;  $\text{I}^-$ , 20461-54-5.

(31) The maximum permissible concentration ratio between the interfering and detecting ions is determined by the reciprocal of the selectivity constant  $K(\text{I}/\text{Br})$  which is calculated from the quotient of the solubility products of the original matrix substance (here  $\text{AgI}$ ) and  $\text{AgBr}$ . For definition of selectivity constant see, for example: Camman, K. *Das Arbeiten mit ionenselektiven Elektroden*; Springer-Verlag: Berlin, 1973; Chapter 1.5.

(32) Reference 27, p 140.

(33) Reference 27, p 460.