CHEMISTRY LETTERS, pp. 1463-1466, 1974. Published by the Chemical Society of Japan

THE MECHANISM OF THE OSCILLATORY DECOMPOSITION OF HYDROGEN PEROXIDE BY THE I_2-IO_3^- COUPLE

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In addition to the second-order back-activatory autocatalytic process $2HIO_2 + HIO + H_2O_2 \longrightarrow 3HIO_2 + H_2O$, which was recently found to be an oscillation source for the oscillatory decomposition of H_2O_2, another similar autocatalytic process $2HIO + H^+ + I^- + H_2O_2 \longrightarrow 3HIO + H_2O$ has been found capable of serving as an oscillation source.

Recently the oscillatory decomposition of the title, discovered by Bray[1] about 50 years ago, was given by us[2] a concrete mechanism whose oscillatory nature was verified by means of computer simulation. The oscillation source of this mechanism consists of a combination of a second-order back-activatory autocatalytic formation of a species with its first-order consumption, which is different from two oscillation sources so far suggested; one is a quadratically branched chain reaction suggested by Degn[3] and the other is a combination of autocatalytic formations of a species with its consumptions of higher orders by Field, Körös, and Noyes.[4] The purpose of this paper is to propose another oscillation source of the same sort as our earlier one.

In view of Ref. 2) being now in due course toward publication, it will first be outlined how the earlier oscillation source was derived. A survey of literature suggests that the oscillatory decomposition is associated with the following six overall reactions, each of which has been investigated considerably

$$2IO_3^- + 2H^+ + 5H_2O_2 \longrightarrow I_2 + 5O_2 + 6H_2O$$
$$I_2 + 5H_2O_2 \longrightarrow 2IO_3^- + 2H^+ + 4H_2O$$
$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$
$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$$
$$I_2 + H_2O \rightleftharpoons HIO + I^- + H^+$$
$$H_2O_2 \longrightarrow H_2O + 0.5O_2$$

and that, if we find a mechanism which can explain all the above reactions mechanistically, the mechanism has high possibility to account for the oscillatory decomposition. In accordance with this suggestion, the sequence of steps, shown in Fig. 1, was first constructed with such species as have been considered to be probable species; in Fig. 1 the lower case letters a, b, c, d, and e are used to indicate the kind of reaction with meanings of reduction by H_2O_2 to generate O_2, oxidation by H_2O_2, disproportionation, hydrolysis, and protonation, respectively. Since the sequence of Fig. 1 contains the first-order autocatalytic process $HIO_2 + HIO + H_2O_2 \longrightarrow 2HIO_2 + H_2O$ as a result of $HIO_2 + HIO \rightleftharpoons H_2I_2O_3$ followed by $H_2I_2O_3 + H_2O_2 \longrightarrow 2HIO_2 + H_2O$ and therefore has possibility[5] to show oscillation, it was subjected to 92 kinds of computer simulations, but without yielding

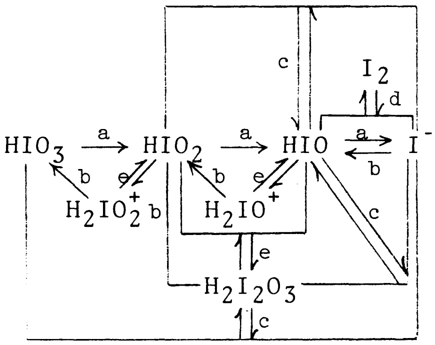

Fig. 1. The sequence of steps first constructed and subjected to computer simulations.

any oscillations. Here we examined oscillatory nature of the sequence of Fig. 2 based on the Higgins rule of thumb,5) and found that n should be higher than 1. Thus we chose 2, the smallest favorable integer, for n and devised an additional sequence of steps shown in Fig. 3 (to be called the first oscillation source in what follows), which results in a second-order back-activatory autocatalytic process $2HIO_2 + HIO + H_2O_2 \longrightarrow 3HIO_2 + H_2O$: The species $H_3I_3O_5$ has not yet been established experimentally, but its formation seems probable since large species6,7) such as $H_2I_3O_{14}^{5-}$ and $H_4I_3O_{14}^{3-}$ are found. Finally

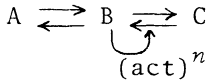

Fig. 2. A basic sequence of steps possible to oscillate. $(act)^n$ denotes the step C $\longrightarrow$ B to be a back-activatory step of nth order in [B]. This is contained in the sequence of Fig. 1 as readily seen if we replace A, B, and C by HIO_3, HIO_2, and HIO, respectively.

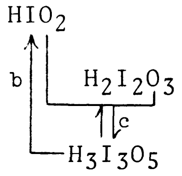

Fig. 3. The additional sequence to the sequence of Fig. 1 —— the 1st oscillation source.

it was examined whether or not the sequence of Fig. 3, when incorporated into that of Fig. 1, would serve as an oscillation source. The combined sequence of steps of Figs. 1 and 3 was reduced to the practical mechanism, shown in Fig. 4, by neglecting minor steps and then subjected to computer simulations. The time courses obtained for $[I_2]$, $[I^-]$, and the rate of O_2 evolution were in qualitative agreement with observations.8) Above has been described the outline of Ref. 2).

To find quantitative agreement with observations, we now advanced our computer simulation by assigning various values on the rate constants in view of experimentally determined values. In these simulations, though limited in number of trials, it was found that the computed synchronization between $[I^-]$ and $[I_2]$, in which both the concentrations decrease simultaneously, could hardly be brought into agreement with the observed one in which the decrease in $[I^-]$ to a minimum is followed by a decrease in $[I_2]$. To reconcile this discrepancy we devised the second possible oscillation source of Fig. 5 with the aid of an additional species $H_3I_3O_2$, which is as probable as $H_3I_3O_5$ mentioned above. As readily seen from comparison of Figs. 3 and 5, the second oscillation source is also a second-order back-activatory autocatalytic process resulting in $2HIO + I^- + H^+ + H_2O_2$ — $3HIO + H_2O$. As with the first oscillation source of Fig. 3, in order to examine whether

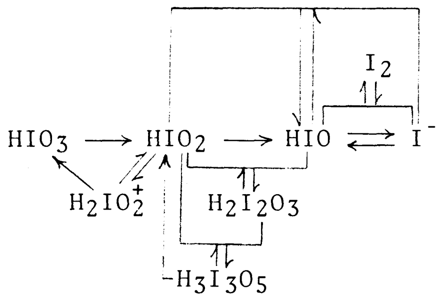

Fig. 4. The practical mechanism.

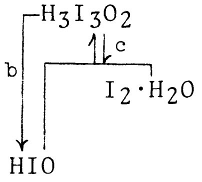

Fig. 5. The second oscillation source. The hydrated iodine would be a better symbol than I_2 in Fig. 1.

or not the second oscillation source can actually produce oscillation when incorporated into the sequence of Fig. 1, the combined sequence of steps of Figs. 1 and 5 was reduced to the simplified mechanism shown in Fig. 6 (without the first oscillation source included), and subjected to computer simulations. An example of oscillation obtained is shown in Fig. 7, in which the synchronization between $[I^-]$ and $[I_2]$ is in semi-quantitative agreement with the observation as mentioned above, and it has thus been confirmed that the second oscillation source is capable of not only causing oscillations but also reconciling the above-mentioned discrepancy.

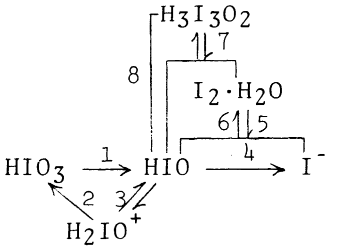

Fig. 6. The simplified mechanism with the second oscillation source.

In order to establish the mechanism, we are now investigating, in detail by means of computer simulations, to what extent both the oscillation sources can reproduce experimental results. However, establishment of the mechanism is not so easy because many of the rate constants for the elementary steps have not yet been determined experimentally and because experimentally determined values of rate constants, if too large, can not be handled by the computer. Under such a circumstance we regard it as a great progress toward understanding complicated oscillatory reactions that two kinds of oscillation sources have been discovered theoretically.

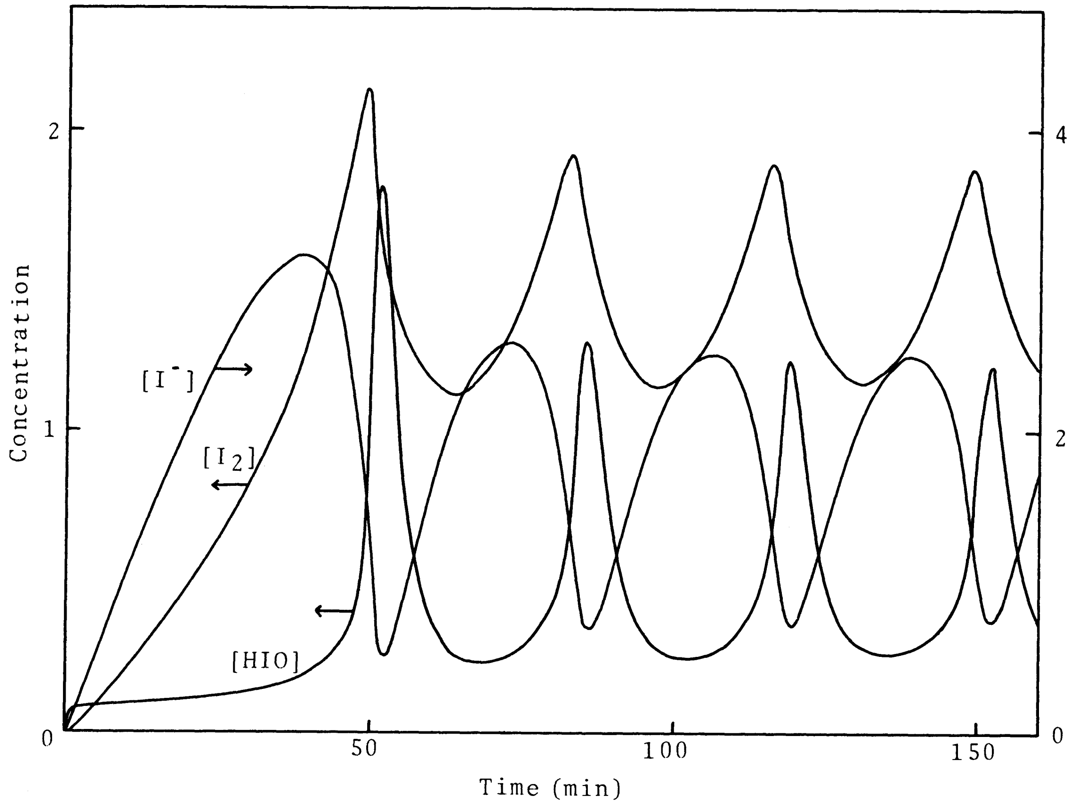

Fig. 7. An example of oscillation which a computer simulation on the mechanism of Fig. 6 yielded. The value of rate, v_i, and rate constant, k_i, for step i adopted are: $v_1=k_1[H_2O_2][HIO_3]=0.2$, $k_{2'}\equiv k_2K_3$x $[H^+][H_2O_2]=0.4$ $(v_2=k_{2'}[HIO])$, $k_4[H_2O_2]=1.5$, $k_5=10$, $k_6[H^+]=20$, and $k_{8'}\equiv k_8K_7[H_2O_2]=1$ $(v_8=k_{8'}[HIO][I_2\cdot H_2O])$, where K_i refers to the equilibrium constant for step i. See Fig. 6 for the step nos. For comparison with experimental results, multiply the value of concentration by $\bar{v}_1/v_1$, where $\bar{v}_1$ is the actual rate of step 1 experimentally given[9] as $\bar{v}_1(\text{mol l}^{-1}\ \text{min}^{-1}) = 2.6\text{x}10^{-4}[HIO_3][H_2O_2] + 129\text{x}10^{-4}[H^+]\text{x}$ $[HIO_3][H_2O_2]$.

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(Received August 28, 1974)