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Modeling the Complex Bromate−Iodine Reaction

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In this article, it is shown that the FLEK model (ref 5) is able to model the experimental results of the bromate−iodine clock reaction. Five different complex chemical systems, the bromate−iodide clock and oscillating reactions, the bromite−iodide clock and oscillating reactions, and now the bromate−iodine clock reaction are adequately accounted for by the FLEK model.

Introduction

Nonlinear phenomena like oscillating and clock reactions have been attracting much attention and are at the center of many vital processes.[1−4] Many of these complex systems involve oxohalogen species possessing different oxidation states and stabilities. Autocatalytic pathways further extend the complexity of these reactions. Rationale of these reactions has been attempted by various researchers and it is quite common that different mechanisms have been proposed for the same clock or oscillating reaction. Several years ago, Faria et al. proposed the FLEK mechanism to account for four different nonlinear reactions: the clock and oscillating reactions for the bromite−iodide and bromate−iodide systems.[5] Three years later, Chinake and Simoyi (CS) proposed for the bromate−iodine reaction a mechanism,[6,7] which differed in several aspects from the FLEK mechanism, despite the fact that this system involves the same bromine and iodine aqueous chemistry. In this article, we present the results of our modeling of the bromate−iodine reaction using the FLEK model, which provides a better agreement with the experimental results than does the CS model.

Theoretical Methods

All calculations were performed using PC compatible computers and a program written by Dr. István Lengyel in *Turbo Pascal 6.0* and adapted to *Free Pascal 2.0.4* to solve autonomous ordinary differential equation systems by a semi-implicit Runge−Kutta method.[8]

The calculations using both the CS and FLEK models were made at constant $[H^+]$ and the background concentration (initial concentration for species not initially present)[9] equal to 1×10^{-10} M.

Results and Discussion

On following the bromate−iodine reaction by UV−vis spectroscopy, two absorptions, at 390 and 460 nm, have particular importance. The main absorbing species at 390 nm are IBr ($\varepsilon = 346$ M^{-1} cm^{-1})[6,10] and Br_2 ($\varepsilon = 161$ M^{-1} cm^{-1})[6] as well as I_2 ($\varepsilon = 176$ M^{-1} cm^{-1}),[10] whereas the isosbestic point of the pair I_2/I_3^- ($\varepsilon = 770$ M^{-1} cm^{-1})[6] occurs at 460 nm. The bromate−iodine reaction was monitored by Chinake and Simoyi[6] from the changes at both wavelengths on changing the initial concentrations of reactants. Their experimental results were accounted for by a mechanism involving 10 independent species and 17 reactions proposed by these authors (CS model).[6] Alternatively, another mechanism comprising 14 independent species and 21 reactions proposed by Faria et al. (FLEK model)[5] can be used to explain the same experimental results. As we show below, the FLEK mechanism provides better agreement than does the CS mechanism. For reasons, which we do not understand, the figures, which we calculated using the CS mechanism, are significantly different from those presented in the original Chinake and Simoyi papers.[6,7]

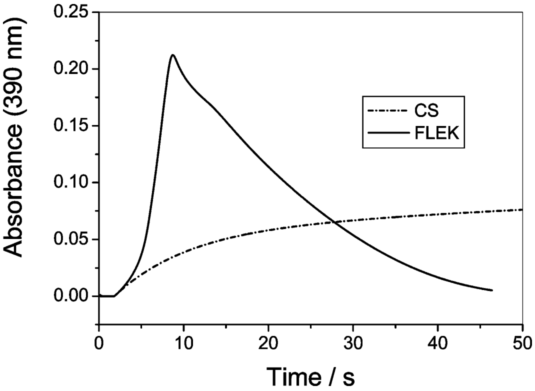

Figure 1. Calculated absorbance at 390 nm for the reaction between $[BrO_3^-]_0 = 1 \times 10^{-2}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M, $[I_2]_0 = 2.05 \times 10^{-4}$ M, $[H^+]_0 = 1.0$ M using CS model[6,7] and FLEK model.[5] This figure must be compared with Figure 18a in ref 6. Only the absorbances of IBr and Br_2 were considered.

Figure 1 shows the calculated changes in absorbance with time using the CS[6,7] and FLEK models at 390 nm for the reaction involving $[BrO_3^-]_0 = 1 \times 10^{-2}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M, $[I_2]_0 = 2.05 \times 10^{-4}$ M, and $[H^+]_0 = 1.0$ M. This figure must be contrasted with figures 18a (ref 6) and 10 (ref 7) and shows that, in our hands, the CS model produces results that are far removed from the experimental results. To produce these figures, we considered, as did Chinake and Simoyi,[6,7] that the main absorbing species at 390 nm were IBr and Br_2. Whereas the agreement for the FLEK model is not perfect, with both the time scale being shorter and the maximum absorbance being lower than observed, the general shape is similar to that found experimentally. Including the iodine absorbance at 390 nm

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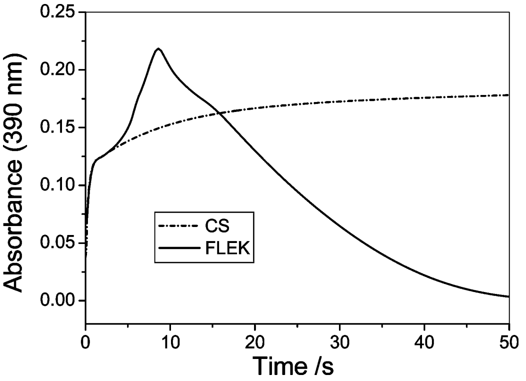

Figure 2. Calculated absorbance at 390 nm for the reaction between $[BrO_3^-]_0 = 1 \times 10^{-2}$ M, $[I^-]_0 = 1 \times 10^{-3}$ M, $[I_2]_0 = 2.05 \times 10^{-4}$ M, $[H^+]_0 = 1.0$ M using CS model[6,7] and FLEK model.[5] This figure must be compared with Figure 18a in ref 6. In addition to IBr and Br_2 absorbances, the absorbance of I_2 were considered too.

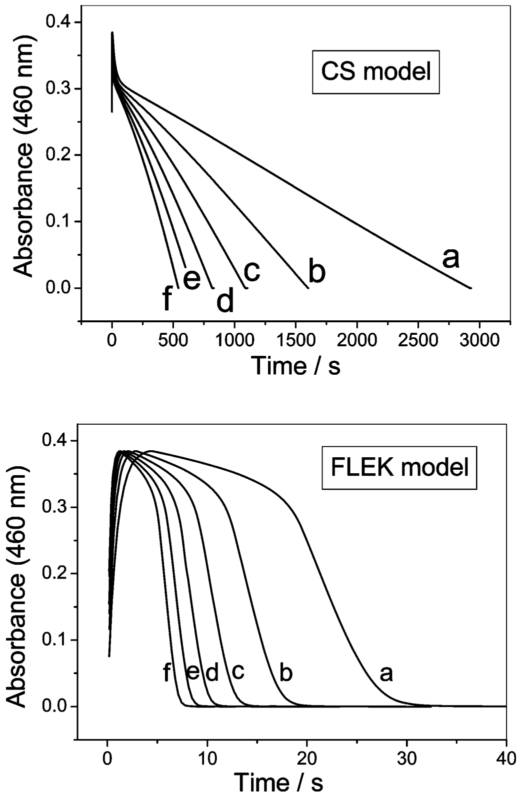

Figure 3. Calculated absorbance at 460 nm on changing the initial bromate concentration on the reaction between $[I^-]_0 = 1 \times 10^{-3}$ M, $[H^+]_0 = 1.5$ M, and $[BrO_3^-]_0 = 2 \times 10^{-3}$ (a), 3×10^{-3} (b), 4×10^{-3} (c), 5×10^{-3} (d), 6×10^{-3} (e), 7×10^{-3} (f), M, using CS model[6,7] and FLEK model.[5] This figure should be compared with Figure 5b in ref 6.

(Figure 2), the FLEK model provides better agreement with the experimental results at the early stages of the reaction; however, the CS model remains unsatisfactory.

Chinake and Simoyi's paper[6] is very rich in experimental results, which can be used as additional tests for modeling this reaction. Figure 3 shows the effect of changing the initial bromate concentration on the calculated absorbance at 460 nm, where the main absorbing species is iodine, using the CS and FLEK models. These results must be compared with the experimental results shown in Figure 5b in ref 6. Again, the FLEK model provides a shorter time scale than that found experimentally. However, the overall profile is much closer to the experimental results than that obtained using the CS model. In addition, the time scale calculated with the CS model is much too long.

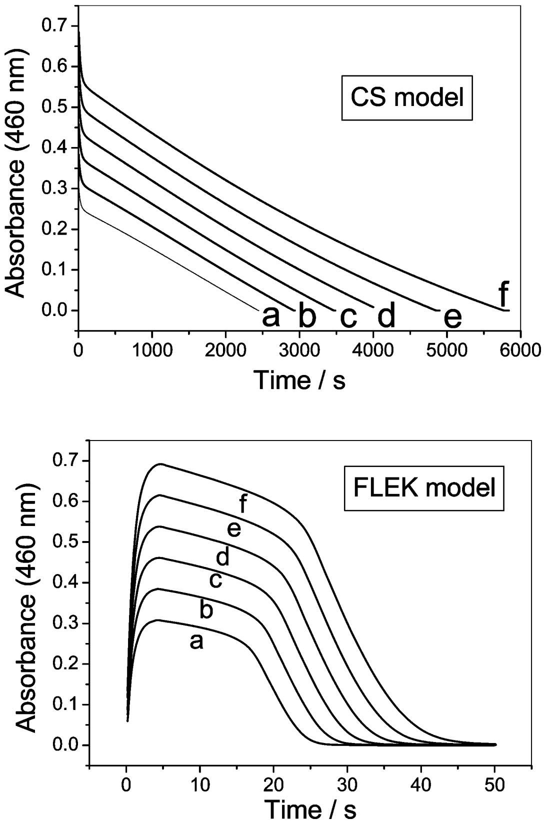

Figure 4. Effect of the initial iodide concentration on the calculated absorbance at 460 nm for the reaction between $[BrO_3^-]_0 = 2 \times 10^{-3}$ M, $[H^+]_0 = 1.5$ M, and $[I^-]_0 = 8 \times 10^{-4}$ (a), 1×10^{-3} (b), 1.2×10^{-3} (c), 1.4×10^{-3} (d), 1.6×10^{-3} (e), 1.8×10^{-3} (f), M, using CS model[6,7] and FLEK model.[5] This figure must be compared with Figure 7b in ref 6.

Figure 4 shows the effect of changing the iodide initial concentration on the calculated absorbance at 460 nm, using the CS and FLEK models. Compared with the experimental results, shown in Figure 7b of ref 6, the FLEK model again calculates a shorter time scale but the overall profile is much closer to the experimental results than the obtained using the CS model.

There are several differences between the FLEK and CS models as is shown in Tables 1 and 2. Because of this, it is difficult to point to only one or two reactions that are responsible for the differences between the two models. However, we can highlight some of the most significant differences. Starting with the bromate reactions, we notice that M2 has a rate constant much lower than that of R18. Values of 1.5×10^2 and 8×10^2 M^{-2} s^{-1} had been used before.[11,12] The FLEK value is greater than these: in contrast the CS value is around 1000 times lower. As $HBrO_2$ is usually considered a very important species as it participates in feedback sequences, the low value used in the CS model may explain the longer time scales observed for this model in Figures 3 and 4.

The rate constant used in the CS model for the reverse M4 reaction is outdated as this value was revised in 1986 to 3.2 M^{-1} s^{-1}, a value now used by many authors.[13,14] This reaction was not included in the FLEK model. As this reaction between two intermediate species, both in low concentrations, has a low rate constant, its exclusion from the FLEK model should not

TABLE 1: CS Model[6] Compared with the FLEK Model[5a]

reaction number[6]	reaction	rate constant in CS model	reaction number and rate constant in FLEK model
M1	$BrO_3^- + I^- + 2H^+ \rightarrow HBrO_2 + HOI$	$44.3\ M^{-3}\ s^{-1}$	(R17) $45\ M^{-3}\ s^{-1}$
M2	$BrO_3^- + HOI + H^+ \rightarrow HBrO_2 + HIO_2$	$2.6 \times 10^{-1}\ M^{-2}\ s^{-1}$	(R18) $8 \times 10^{3}\ M^{-2}\ s^{-1}$
M3	$BrO_3^- + HIO_2 \rightarrow IO_3^- + HBrO_2$	$9\ M^{-1}\ s^{-1}$	(R19) $10\ M^{-1}\ s^{-1}$
M4	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$2.1\ M^{-3}\ s^{-1}$	(R20) $2\ M^{-3}\ s^{-1}$
$M4_{rev}$	$HBrO_2 + HOBr \rightarrow BrO_3^- + Br^- + 2H^+$	$1 \times 10^{4}\ M^{-1}\ s^{-1}$	absent
M5	$BrO_3^- + IBr + H_2O \rightarrow IO_3^- + Br^- + HOBr + H^+$	$8 \times 10^{-4}\ M^{-1}\ s^{-1}$	absent
M6	$HBrO_2 + HOI \rightarrow HIO_2 + HOBr$	$2.5 \times 10^{8}\ M^{-1}\ s^{-1}$	(R3) $6 \times 10^{7}\ M^{-1}\ s^{-1}$
M7	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$2 \times 10^{6}\ M^{-2}\ s^{-1}$	(R4) $2 \times 10^{6}\ M^{-2}\ s^{-1}$
M8	$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$	$2.2 \times 10^{2}\ M^{-1}\ s^{-1}$	(R5) $2.2 \times 10^{3}\ M^{-1}\ s^{-1}$
M9	$HOBr + I_2 \rightarrow HOI + IBr$	$8 \times 10^{8}\ M^{-1}\ s^{-1}$	(R13) $1 \times 10^{7}\ M^{-1}\ s^{-1}$
$M9_{rev}$	$HOI + IBr \rightarrow HOBr + I_2$	$1 \times 10^{2}\ M^{-1}\ s^{-1}$	absent
M10	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	$4.1 \times 10^{9}\ M^{-2}\ s^{-1}$	absent
$M10_{rev}$	$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$	$1.1 \times 10^{2}\ s^{-1}$	absent
M11	$HOBr + HIO_2 \rightarrow IO_3^- + Br^- + 2H^+$	$1 \times 10^{6}\ M^{-1}\ s^{-1}$	(R7) $1 \times 10^{6}\ M^{-1}\ s^{-1}$
M12	$HOBr + HOI \rightarrow Br^- + HIO_2 + H^+$	$1 \times 10^{6}\ M^{-1}\ s^{-1}$	(R6) $1 \times 10^{6}\ M^{-1}\ s^{-1}$
M13	$HIO_2 + HOI \rightarrow IO_3^- + I^- + 2H^+$	$6 \times 10^{2}\ M^{-1}\ s^{-1}$	(R10) $6 \times 10^{3}\ M^{-1}\ s^{-1}$
M14	$I^- + HOI + H^+ \rightarrow I_2 + H_2O$	$3.1 \times 10^{12}\ M^{-2}\ s^{-1}$	(R15) + (R16)
$M14_{rev}$	$I_2 + H_2O \rightarrow I^- + HOI + H^+$	$2.2\ s^{-1}$	(R15) + (R16)
M15	$IBr + H_2O \rightarrow HOI + Br^- + H^+$	$8 \times 10^{-1}\ s^{-1}$	(R11) $8 \times 10^{5}\ s^{-1}$
$M15_{rev}$	$HOI + Br^- + H^+ \rightarrow IBr + H_2O$	$1 \times 10^{8}\ M^{-2}\ s^{-1}$	(R11) $4.1 \times 10^{12}\ M^{-2}\ s^{-1}$
M16	$IBr + I^- \rightarrow I_2 + Br^-$	$2 \times 10^{10}\ M^{-1}\ s^{-1}$	(R14) $2 \times 10^{9}\ M^{-1}\ s^{-1}$
$M16_{rev}$	$I_2 + Br^- \rightarrow IBr + I^-$	$4.74 \times 10^{2}\ M^{-1}\ s^{-1}$	(R14) $4.74 \times 10^{3}\ M^{-1}\ s^{-1}$
M17	$Br_2 + I_2 \rightarrow 2IBr$	$1.3 \times 10^{5}\ M^{-1}\ s^{-1}$	absent
$M17_{rev}$	$2IBr \rightarrow Br_2 + I_2$	$1.0\ M^{-1}\ s^{-1}$	absent

[a] Numbering of the reactions is the same used in the CS original paper. The last column presents the rate constant values used in the FLEK model.

TABLE 2: FLEK Model[5] Compared with the CS Model[6a]

reaction number[5]	reaction	rate constant in FLEK model	reaction number and rate constant in CS model
R1	$HBrO_2 \rightarrow BrO_2^- + H^+$	$3.73 \times 10^{6}\ s^{-1}$	absent
$R1_{rev}$	$BrO_2^- + H^+ \rightarrow HBrO_2$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	absent
R2	$HBrO_2 + HOI \rightarrow HOBr + HIO_2$	$6 \times 10^{7}\ M^{-1}\ s^{-1}$	absent
R3	$HBrO_2 + HOI \rightarrow HIO_2 + HOBr$	$6 \times 10^{7}\ M^{-1}\ s^{-1}$	(M6) $2.5 \times 10^{8}\ M^{-1}\ s^{-1}$
R4	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$2 \times 10^{6}\ M^{-2}\ s^{-1}$	(M7) $2 \times 10^{6}\ M^{-2}\ s^{-1}$
R5	$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$	$2.2 \times 10^{3}\ M^{-1}\ s^{-1}$	(M8) $2.2 \times 10^{2}\ M^{-1}\ s^{-1}$
R6	$HOBr + HOI \rightarrow Br^- + HIO_2 + H^+$	$1 \times 10^{6}\ M^{-1}\ s^{-1}$	(M12) $1 \times 10^{6}\ M^{-1}\ s^{-1}$
R7	$HOBr + HIO_2 \rightarrow IO_3^- + Br^- + 2H^+$	$1 \times 10^{6}\ M^{-1}\ s^{-1}$	(M11) $1 \times 10^{6}\ M^{-1}\ s^{-1}$
R8	$HOBr \rightarrow H^+ + BrO^-$	$15.8\ s^{-1}$	absent
$R8_{rev}$	$H^+ + BrO^- \rightarrow HOBr$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	absent
R9	$HIO_2 + I^- \rightarrow HOI + IO^-\ (\rightarrow HOI)$	$2 \times 10^{5}\ M^{-1}\ s^{-1}$	absent
R10	$HIO_2 + HOI \rightarrow IO_3^- + I^- + 2H^+$	$6 \times 10^{3}\ M^{-1}\ s^{-1}$	(M13) $6 \times 10^{2}\ M^{-1}\ s^{-1}$
R11	$IBr + H_2O \rightarrow HOI + Br^- + H^+$	$8 \times 10^{5}\ s^{-1}$	(M15) $8 \times 10^{-1}\ s^{-1}$
$R11_{rev}$	$HOI + Br^- + H^+ \rightarrow IBr + H_2O$	$4.1 \times 10^{12}\ M^{-2}\ s^{-1}$	(M15) $1 \times 10^{8}\ M^{-2}\ s^{-1}$
R12	$HOBr + I^- \rightarrow IBr + OH^-$	$5 \times 10^{9}\ M^{-1}\ s^{-1}$	absent
R13	$HOBr + I_2 \rightarrow HOI + IBr$	$1 \times 10^{7}\ M^{-1}\ s^{-1}$	(M9) $8 \times 10^{8}\ M^{-1}\ s^{-1}$
R14	$IBr + I^- \rightarrow I_2 + Br^-$	$2 \times 10^{9}\ M^{-1}\ s^{-1}$	(M16) $2 \times 10^{10}\ M^{-1}\ s^{-1}$
$R14_{rev}$	$I_2 + Br^- \rightarrow IBr + I^-$	$4.74 \times 10^{3}\ M^{-1}\ s^{-1}$	(M16) $4.74 \times 10^{2}\ M^{-1}\ s^{-1}$
R15	$I_2 + OH^- \rightarrow I_2OH^-$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	absent
$R15_{rev}$	$I_2OH^- \rightarrow I_2 + OH^-$	$6 \times 10^{5}\ s^{-1}$	absent
R16	$I_2OH^- \rightarrow HOI + I^-$	$6 \times 10^{3}\ s^{-1}$	absent
$R16_{rev}$	$HOI + I^- \rightarrow I_2OH^-$	$2.5 \times 10^{6}\ M^{-1}\ s^{-1}$	absent
R17	$BrO_3^- + I^- + 2H^+ \rightarrow HBrO_2 + HOI$	$45\ M^{-3}\ s^{-1}$	(M1) $44.3\ M^{-3}\ s^{-1}$
R18	$BrO_3^- + HOI + H^+ \rightarrow HBrO_2 + HIO_2$	$8 \times 10^{3}\ M^{-2}\ s^{-1}$	(M2) $2.6 \times 10^{-1}\ M^{-2}\ s^{-1}$
R19	$BrO_3^- + HIO_2 \rightarrow IO_3^- + HBrO_2$	$10\ M^{-1}\ s^{-1}$	(M3) $9\ M^{-1}\ s^{-1}$
R20	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$2\ M^{-3}\ s^{-1}$	(M4) $2.1\ M^{-3}\ s^{-1}$

[a] Numbering of the reactions follows that used in the FLEK original paper. The last column presents the rate constant values used in the CS model. The water dissociation equilibrium was not used because $[H^+]$ was considered fixed as its concentration is high.

be significant but its inclusion in the CS model, because of the high rate constant, will have a major influence.

The M5 reaction in the CS model has a very low rate constant and the presence of this reaction in the model should not be very significant. It was not included in the FLEK model. The M5 step, being an overall transfer of three oxygen atoms from bromate to iodine, certainly will involve several intermediate steps. Formation of HOBr, another very important species in feedback sequences, does not depend solely on this reaction, as it can be produced by reactions M4/R20, M6/R3, and M7/R4.

Turning now to the $HBrO_2$ reactions, the FLEK model includes the reaction (R2) between two intermediates ($HBrO_2$ and HOI) with a high rate constant ($6 \times 10^{7}\ M^{-1}\ s^{-1}$, experimental value from Kern and Kim[15]). As this reaction also produces HOBr, which is a very important feedback species, it certainly contributes to the different results of the FLEK and CS models.

Another reaction involving $HBrO_2$ is its disproportionation (M8/R5). FLEK uses the experimental value of 2.2×10^3 M^{-1} s^{-1} from Ariese and Ungvárai-Nagy[16] for 0.5 M H_2SO_4 at 24 °C. More recently, Försterling and Varga[17] determined this rate constant at different sulfuric acid concentrations and found that it increases as the acid concentration increases, rising from 2.2×10^3 M^{-1} s^{-1} at $[H_2SO_4] = 0.5$ M to 6.5×10^3 M^{-1} s^{-1} at $[H_2SO_4] = 1.5$ M. As in the CS model, the FLEK model ignored this acidity effect but there is no basis for the value of 2.2×10^2 M^{-1} s^{-1} used in the CS model. This 10-fold difference between the values used in the CS and FLEK models can contribute to the different behaviors observed between these two models.

Reactions R1 and R8, including their reverse reactions, account for the pK_a of $HBrO_2$ and HOBr. These reactions are not present in the CS model but cannot be responsible for the different behavior between these models as at the high $[H^+]$ employed in the experiments both acids are completely protonated.

For the HOBr reactions, the main differences are in reactions M10 (present only in the CS model) and R12 (present only in the FLEK model). Both have very high rate constants and are important in both mechanisms. In the FLEK model, the R12 reaction produces IBr directly. Otherwise, the CS model goes through bromine formation by M10, followed by M17 to obtain IBr. Thus, IBr is formed by different routes in the two mechanisms. In the FLEK model, an experimental rate constant value for R12 is used.[18] In the CS model, initially the Eigen and Kustin[19] value ($k_{M10} = 1.6 \times 10^{10}$ M^{-2} s^{-1}) was used but the final value used, 4.1×10^9 M^{-2} s^{-1} is four times lower, given an equilibrium constant for bromine hydrolysis of 2.7×10^{-8} M^2. For comparison, the Eigen and Kustin[19] equilibrium constant value is $K = 6.9 \times 10^{-9}$ M^2 (25 °C, $\mu = 0.1$ M) and a more recent value from Beckwith et al.[20] is $K = 6.2 \times 10^{-9}$ (25 °C, $\mu = 1.00$ M). These values show that the bromine hydrolysis in the CS model is shifted to produce less bromine than if a correct equilibrium constant had been used.

As IBr is a central species in both mechanisms, the set of reactions that produces and consumes this species is very important. Both the CS and FLEK models include the equilibrium $IBr + I^- \rightleftarrows I_2 + Br^-$ (M16/M16$_{rev}$ and R14/R14$_{rev}$ respectively). The forward reaction in the FLEK model uses the experimental rate constant of 2×10^9 M^{-1} s^{-1} determined by Troy et al.[21] but the CS model uses a value 10 times greater. In addition, the reverse rate constant in the FLEK model produces an equilibrium constant ($K_{R14} = 4.2 \times 10^5$), in good agreement with the value calculated from the $\Delta_f G°$ value ($K = 4.1 \times 10^5$).[22] However, the equilibrium constant for this reaction in the CS model is significantly higher, $K_{M16} = 4.2 \times 10^7$, which can be a further reason for the poorer fitting CS model.

Another important reaction is the IBr hydrolysis equilibrium (M15/M15$_{rev}$, R11/R11$_{rev}$). The rate constants used in the CS and FLEK models are very different. The FLEK model uses the experimental rate constant of 8×10^5 s^{-1} determined by Troy et al.[21] for the forward reaction, and the reverse reaction rate constant value will produce an equilibrium constant $K_{R11} = 2.0 \times 10^{-7}$ M^2 in close agreement with the experimental value of $K_{exp} = 2.4 \times 10^{-7}$ M^2.[21] However, the equilibrium constant in the CS model is $K_{M15} = 2.0 \times 10^{-9}$ M^2.

On the basis of these differences between the models, one reaction or rate constant cannot be responsible for their different results. As the FLEK model produces results closer to experimental values than does the CS model, we can conclude that the use of more experimental values in the FLEK model results in the better agreement. If we have to point out the main causes for the differences between the two models, we would suggest the rate constants (and equilibrium constant) for IBr hydrolysis and formation, the disproportionation of $HBrO_2$, and its reaction with HOI (which was not included in CS model).

Conclusions

The FLEK (Faria et al.)[5] model provides better agreement than does the CS (Chinake and Simoyi)[6] model with experimental results for complex chemical systems, such as the clock reactions and oscillating reactions for the systems bromite−iodide, bromate−iodide, and the bromate−iodine system, which behaves as a clock reaction under certain experimental conditions.

While progress has clearly been made, we are not yet in the position to forecast the behavior of all oxobromine and oxoiodine systems in aqueous solution, including nonoxygenated species such as I_2 and IBr. Only the modeling of additional systems using the same set of reactions can give us the confidence about the interplay of these reactions and rate constants employed.

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