Comment on "Belousov−Zhabotinsky Oscillations in Bromate−Oxalic Acid−$MnSO_4$−H_2SO_4−Acetone System in Nonionic Surfactant Medium. A Calorimetric Study"

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S. Biswas et al.[1] have recently studied the thermal oscillations in an oxalic acid−bromate−$MnSO_4$−H_2SO_4−acetone system in aqueous solution of nonionic surfactants, TX-100, Tweens (20, 40, and 60), and Brijs (56, 58, and 76). They observed that significantly low concentration of the surfactants can inhibit the oscillatory reaction.

We should like to notice that nonionic surfactant Triton X-100 {(*p-tert*-octylphenoxy)polyoxyethylene (9.5) ether} is probably not an inert substance in the BZ system. Triton X-100 can react with bromate in aqueous sulfuric acid solution to form a molecular bromine. (We have not examined the reactivity of the Tweens and Brijs.)

In our experiments we used the same concentrations of reactants as in the work of Biswas et al.[1] Sodium bromate, Triton X-100, and sulfuric acid were of commercial analytical quality (Merck, Germany) and used without further purification. Deionized water was used to prepare all solutions. Kinetic experiments were carried out spectrophotometrically by recording the changes in the Br_2 absorbance at 400 nm where Br_2 is the major absorbing species (molar absorbance coefficient $\epsilon = 166$ M^{-1} cm^{-1}) with a computer-controlled Hitachi model U-2001 UV−Vis spectrophotometer. The reactant mixture contained H_2SO_4 and $NaBrO_3$, and the reaction was started by the final rapid addition of TX-100 into the photometric closed cell of 5 cm optical path.

Typical kinetic curves are shown in Figure 1. The molecular bromine was formed very rapidly in the first stage of the reaction, and the absorbance reached its maximum value within 20, 130, and 500 s at $[H_2SO_4]_o = 2.5$, 1.25, and 0.625 mol·dm^{-3}, respectively. The amount of the formed Br_2 has been measured at different concentrations of TX-100 and at three different concentrations of H_2SO_4. The data are given in Table 1. The concentration of Br_2 increases with increasing concentration of TX-100, and the slope of this linear dependence is equal to 2.24.

It can be seen from Figure 1 that the concentration of Br_2 decreases exponentially during the further course of the reaction. The rate of Br_2 disappearance at higher $[H_2SO_4]$ may be described by the first-order kinetic law. The observed pseudo-first-order rate constants for sulfuric acid concentrations 1.25 and 2.5 M are $k = 2.53 \times 10^{-3}$ s^{-1} and $k = 2.08 \times 10^{-2}$ s^{-1}, respectively (for 0.14 M $NaBrO_3$ and 2×10^{-4} M TX-100, at 30 °C).

At the end of the reaction we can observe the presence of a slight precipitate forming on the bottom of the cell.

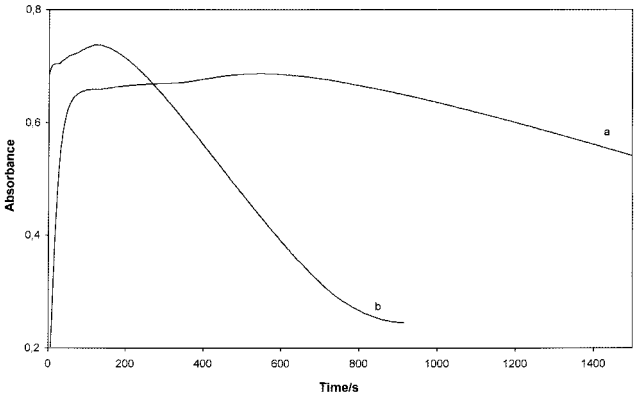

Figure 1. Absorbance at 400 nm vs time during the reaction of bromate with TX-100 in (a) 0.625 M and (b) 1.25 M H_2SO_4. The absorbance is mainly due to Br_2. Initial concentrations: $[NaBrO_3] = 0.14$ M, $[\text{TX-100}] = 4 \times 10^{-4}$ M.

TABLE 1: Amount of Br_2 {$[Br_2]$ M} Formed during the Reaction of BrO_3^- with TX-100[a]

	$[H_2SO_4]$		
[TX-100] M	0.625	1.25	2.5
1×10^{-4}	2.24×10^{-4}	2.55×10^{-4}	2.25×10^{-4}
2×10^{-4}	4.38×10^{-4}	5.06×10^{-4}	5.1×10^{-4}
3.6×10^{-4}	8.02×10^{-4}	7.98×10^{-4}	8.5×10^{-4}
4.0×10^{-4}	8.90×10^{-4}	8.90×10^{-4}	8.7×10^{-4}

[a] $[NaBrO_3] = 0.14$ M.

The BrO_3^-−TX-100 reaction seems to have all the properties that are needed for the generation of nonlinear kinetics. There are at least three reactions that may couple to produce the observed reaction dynamics. By analogy to similar systems[2−4] these reactions could be the oxidation of TX-100 by BrO_3^-, the formation of Br_2, and consumption of Br_2 by the TX-100 and by other organic compounds formed in the reaction of Br_2 with TX-100.

The results of the experiments on the Br_2−TX-100 reaction indicate that it is a relatively very fast reaction and therefore a significant amount of Br_2 cannot be accumulated in the BrO_3^-−TX-100 system until TX-100 is completely oxidized to another organic product. Hence, in a few seconds of the BrO_3^-−TX-100 reaction, there will be probably no TX-100 left in solution.

Our experimental results suggest that the inhibitory effect of nonionic surfactant TX-100 on the BZ oscillatory reaction can be complex and seems not to be straightforward in this regard.

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References and Notes

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