

COMMENTS

New Experimental Data on the Chlorite–Thiourea Reaction¹

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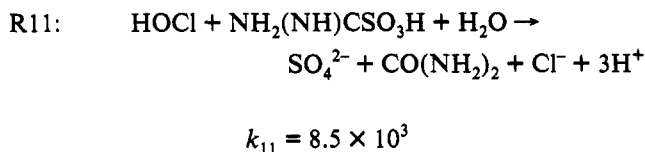
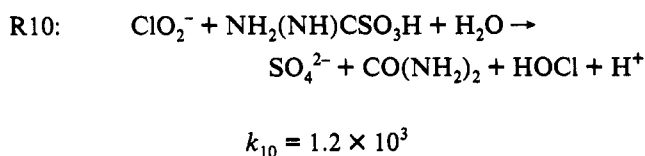
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The chlorite–thiourea reaction has shown some of the most fascinating dynamics of any reaction in chemistry.² In a batch environment it shows clock reaction characteristics in which there is initially a quiescent period before formation of chlorine dioxide. In a continuously stirred tank reactor (CSTR) it shows oscillatory behavior in the redox potential of the reactor which might be described as “chaotic”.³ Lately, we have also discovered that in a tube or a petri dish it produces a wave of chemical reactivity which is triggered from some point of perturbation in the solution.⁴

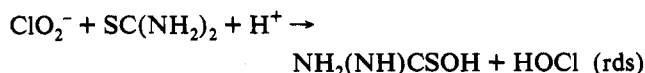
It is because of this wide range of nonlinear behavior that some of us proceeded to attempt to decipher the kinetics and mechanism of the chlorite–thiourea reaction.² We proposed a 13-step reaction mechanism whose most significant features are an autocatalytic production of the sulfonyl acid via a dimer (dithiobisformamidine) and oxidation of thiourea by successive addition of oxygen on the sulfur to give sulfonyl, sulfinic, and sulfonic acids. From barium chloride experiments it was evident that the cleavage of the sulfur–carbon bond to give sulfate and urea occurs after the formation of the sulfonic acid.⁴

This mechanism was able to simulate the batch behavior quite well, especially the length of the induction period. Our further investigations now show that the mechanism cannot satisfactorily simulate the CSTR behavior.

Our work and others seem to question the choice of the rate constants for the following reactions:^{5,6}



It has been generally accepted that the rate-determining step (rds) is the formation of the sulfonyl acid, with further oxygen additions being relatively easy:²



Other work performed on thiourea oxidation by bromine had suggested otherwise.⁷ In the bromine–thiourea reaction the first part of the reaction that produces the sulfonyl acid is very fast and diffusion controlled ($k > 10^9 \text{ M}^{-1} \text{ s}^{-1}$), while the next step,

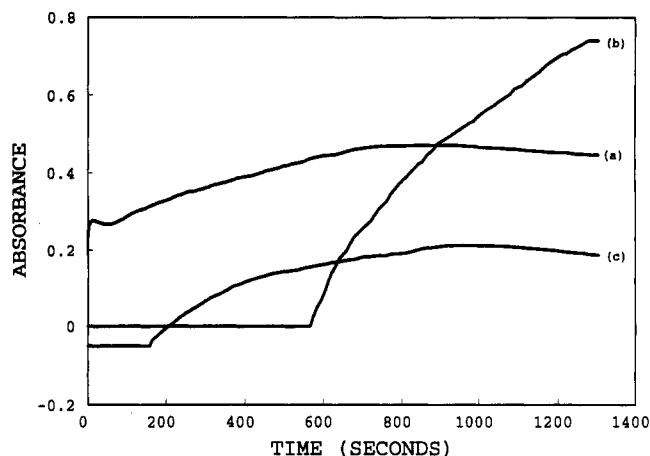


Figure 1. Absorption traces at 360 nm of the reaction of chlorite with (a) AIMSA, (b) AMSA, and (c) thiourea. $[\text{ClO}_2^-]_0 = 0.004 \text{ M}$, and the initial concentration of each of the reductants is 0.001 M . Reaction temperature was $25 \text{ }^\circ\text{C}$, and the ionic strength was 0.5 M (NaClO_4).

the oxidation of the sulfonyl acid to sulfinic acid, is comparatively slow with a bimolecular rate constant of only $27.8 \text{ M}^{-1} \text{ s}^{-1}$.

The formation of chlorine dioxide coincides with a sudden decrease in pH and a sudden formation of sulfate, all of which seemed to suggest that R10 and R11 (or any oxidation of the sulfonyl acid to sulfate) are fast and irreversible.

Our present studies show that the mechanism we suggested in ref 2 also cannot adequately describe the traveling wave of chlorine dioxide we observe in the chlorite–thiourea reaction.⁵ This could be because of a bad choice of reaction steps or poor estimation of the relevant kinetics parameters of some of the reaction steps. Of particular note is the fact that the wave front is not sharp but contains a clearly observable reaction zone which precedes the reacted zone.⁵ The reaction zone can be observed by using an acid–base indicator but cannot be observed when barium chloride⁴ and starch are used as indicators.⁵

The observation of a finite reaction zone suggests a region in the chemical wave that is dominated by chemical kinetics. This leads to the belief that the relevant rate constants that control the formation of sulfate from sulfonic acid may not be that high.

We have now accumulated more data that suggest that a revision of k_{10} and k_{11} is necessary:

(a) The aminoiminomethanesulfinic acid, $\text{NH}_2(\text{NH})\text{CSO}_2\text{H}$ (AIMSA), which is one of the proposed intermediates in the oxidation of thiourea to sulfate, was reacted with chlorite, and the same type of behavior was observed as with thiourea itself, clock reaction characteristics, traveling waves, as well as spatiotemporal behavior.⁸

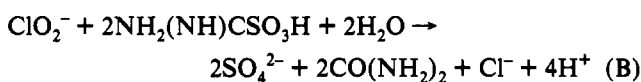
(b) A sulfonic acid, aminomethanesulfonic acid, $\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$ (AMSA), was also reacted with chlorite, and the reaction was not as fast as predicted by k_{10} and k_{11} . Figure 1 shows the absorbance traces obtained with chlorite and thiourea, AIMSA, and AMSA. The longest induction time was obtained with the sulfonic acid.⁸

(c) Recent work by Rabai et al. have shown that the reaction of chlorine dioxide with thiourea yields dithiobisformamidine ion, $(\text{NH}_2)\text{CSSC}(\text{NH}_2)^{2+}$, or AIMSA, depending on initial ratio of chlorine dioxide to thiourea.⁹ The sulfonic acid is formed only in high acid, and there is negligible reaction after that to give sulfate.

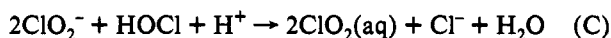
(d) We have run some experiments in which we monitor the rate of consumption of the reductants. Thiourea has an absorption

peak at 268 nm, AIMSAs at 270 nm, and AMSA at 272 nm. ClO_2 and the intermediate¹⁰ Cl_2O_2 also absorb at 270 nm, making it difficult to determine the rate constants from this spectrophotometric method. The rate of oxidation of the sulfonic acid was very slow, signifying rate constants that are at least an order of magnitude smaller than those reported in ref 2.

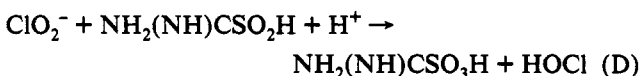
These results indicate that the reaction of chlorite and thiourea can be divided into two parts: the first stage which gives the sulfonic acid and the second stage which takes the sulfonic acid to sulfate.



Addition of reactions A and B gives the overall stoichiometry of the reaction. Setting up the reaction in the form of these two stages can explain why formation of sulfate coincides with a rapid decrease in pH. Formation of ClO_2 at this point can be explained from recent results of Rabai et al. that conclude that the sulfonic acid reacts very slowly with chlorine dioxide.⁹ Without a reductant to consume chlorine dioxide, it accumulates. The major reaction which produces ClO_2 is¹¹



HOCl is formed from the reduction of ClO_2^- , which also explains the long induction period when ClO_2^- oxidizes the sulfonic acid, AMSA. With the slow ClO_2^- -AMSA reaction, the rate of formation of HOCl is very slow, and hence, for a long period of time, no appreciable amount of ClO_2 is formed. The reaction with the sulfonic acid is fastest in producing ClO_2 because the reaction of ClO_2^- with AIMSAs is rapid enough to produce appreciable concentrations of HOCl :



HOCl can react with ClO_2^- as in (C), above, or with remaining AIMSAs. Any ClO_2 formed according to (C) will be consumed

very slowly, and thus ClO_2 accumulates rapidly. Accumulation of ClO_2 ceases when all the AIMSAs have been consumed, and then one observes the slow consumption of ClO_2 by the sulfonic acid. The small ClO_2 peak observed in Figure 1 at the beginning of the reaction can be explained by the fact that all the AIMSAs would not have been consumed at this point.

Accumulation of all this new data allows the following conclusions:

(a) Formation of ClO_2 does not imply that all the sulfur compound has been oxidized to sulfate.

(b) The values of k_{10} and k_{11} are much lower than the values we reported in ref 2. Using new experimental data coupled with computer simulation results, we deduce the following:

$$k_{10} = 2.0 \pm 0.50 \text{ M}^{-1} \text{ s}^{-1} \quad \text{and} \quad k_{11} = 25.0 \pm 7.0 \text{ M}^{-1} \text{ s}^{-1}$$

(c) The traveling wave front is dominated by the kinetics of the sulfonic acid/chlorite/chlorine dioxide reaction network.

(d) Production of ClO_2 , H^+ , and SO_4^{2-} is not sudden and instantaneous, but gradual. Although the decrease in pH is rapid (Figure 1, ref 2), the actual increase in $[\text{H}^+]$ is small.

The importance of this reaction in the generation of nonlinear phenomena in chemistry dictates that, as accurately as possible, rate constants for relevant reaction steps be deduced.

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References and Notes

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