Reaction of Thiourea with Hydrogen Peroxide: ^{13}C NMR Studies of an Oxidative/Reductive Bleaching Process

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ABSTRACT

Thiourea's reaction with hydrogen peroxide in solution under bleaching conditions at three different pH values has been investigated using ^{13}C NMR spectroscopy. Since this reaction is fast and exothermic, it is essential that short total acquisition times be used to accumulate sufficient data to detect different species formed during the reaction. As the abundance of ^{13}C in the reactants in the concentration range studied is very low, ^{13}C-labeled thiourea was used as the starting material. Sufficient data were accumulated in short acquisition times (2–4 minutes) to identify different species formed during the reaction. The results showed that different intermediate products are formed during the reactions, depending on the pH of the medium and the molar ratio of the reactants. The reaction goes through a thiourea dioxide intermediate; this then hydrolyzes under heat and neutral or alkaline conditions to yield sulfinate anion and urea if the initial reaction of thiourea with hydrogen peroxide is allowed to take place in acidic/neutral medium (pH = 4.0–7.0). Because thiourea dioxide hydrolyzes in solution, there is a rapid change in redox potential from a positive value to a high negative value. The species causing the negative redox potential, and hence the species responsible for reductive bleaching, is believed to be the sulfinate anion. The reaction of thiourea with hydrogen peroxide in hydrochloric acid at pH < 1 results in the formation of formamidine disulfide dihydrochloride, which decomposes at pH values greater than 1.

There is a vast amount of information available on the reactions of thiourea with oxidizing agents [4, 5, 18, 20, 21, 23, 24]. The action of hydrogen peroxide on thiourea (Th, Figure 1) was investigated as long ago as 1910, when Barnett [4] concluded that the resultant product depends very much on the pH and conditions of the reaction medium. Unless special precautions are taken, hydrogen peroxide decomposes thiourea into ammonia, carbon dioxide, sulfur, and sulfuric acid [13, 18]. Under closely controlled neutral conditions, Barnett [4] and others [6, 9, 16, 17] produced formamidinesulfinic acid (thiourea dioxide, ThDO, Figure 1) when they added finely powdered thiourea to an aqueous solution of hydrogen peroxide at 0–10°C under different compositions and conditions. Other workers, however, obtained formamidine disulfide (FDS, Figure 1) dihydrochloride by oxidation of thiourea with hydrogen peroxide under strongly acidic (hydrochloric acid, pH < 1) conditions [10, 19, 21]. Marshall [18] reported that the salts of formamidine disulfide are not very stable, and their solutions decompose, especially on warming, with formation of sulfur, thiourea, cyanamide, and free acid. A corresponding decomposition results immediately with the addition of alkali, and this constitutes a very characteristic reaction for these salts. Grigorova and Wright [12] reported that under strong oxidizing conditions, formamidine disulfide oxidizes to cyanamide, hydro-

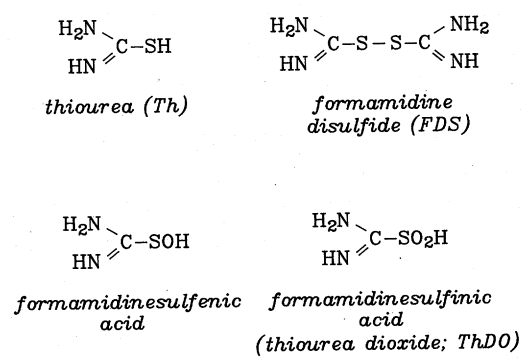

FIGURE 1. Chemical structures of some of the cited sulfur species.

gen sulfide, and elemental sulfur, whereas under mild conditions, it decomposes to thiourea, elemental sulfur, and cyanamide. Hoffmann and Edwards [14] studied the kinetics and mechanism of the oxidation of thiourea with hydrogen peroxide to the formamidine disulfide cation in acid solution. In their study, the rate law and other data indicated that the reactions proceed through nucleophilic displacement by sulfur on oxygen.

We are interested in the reaction of thiourea with hydrogen peroxide because the reaction under certain conditions [1] gives rise to a powerful reductive bleaching agent that may be used either on its own [7] or in combination with an oxidative bleach [1–3, 8, 22]. The bleaching process we developed in earlier work [1–3], in particular, uses the reductive bleach made *in situ* by reaction of thiourea with residual hydrogen peroxide (a range of molar ratios of reactants) from an earlier oxidative bleaching step. We now have used ^{13}C NMR spectroscopy to investigate the various products that arise from the reaction of thiourea with hydrogen peroxide at 60°C under the bleaching conditions we reported earlier [1–3].

Experimental

Thiourea[3] (^{13}C labeled) was obtained from Isotec, Inc.[4], Miamisburg, OH. The hydrogen peroxide was a 30% (w/w) aqueous solution obtained from Mallinckrodt, Inc., Paris, KY. Thiourea dioxide, formamidine disulfide dihydrochloride and tetrasodium pyrophosphate decahydrate were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI. Prestogen NB-W, an activator for hydrogen peroxide under acidic conditions, was supplied by BASF Chemicals Division, Charlotte, NC. All other chemicals used were of ACS grade.

All ^{13}C NMR experiments were run at 60°C on either a JEOL GX-400 (100 MHz for ^{13}C) or a Bruker MSL-300 (75.5 MHz for ^{13}C) using pulse widths of 45°. The sweep widths were 20,000 Hz. Data points (8K) were collected and zero filled (to 16K). The recycle time was 5 seconds, and for ^{13}C-labeled materials 16 or 32 scans were collected. For unlabeled materials, 1024 or 2048 scans were collected. All samples were run in H_2O in the unlocked mode. All chemical shifts are reported as ppm from TMS.

Reaction of thiourea with hydrogen peroxide in solution in the absence of any substrate was run under conditions simulating those of actual bleaching. Stock solutions (alkaline hydrogen peroxide bleach with sodium pyrophosphate decahydrate as stabilizer, pH = 9.2, and acidic hydrogen peroxide bleach with Prestogen NB-W as activator, pH = 5.5) were prepared in the same concentrations as those of alkaline and acidic oxidative bleach baths, but without a nonionic wetting agent that would normally be present in a bleach bath. The pH and redox potential measurements were monitored continuously to make certain that these parameters were kept in accordance with bleaching conditions. Stock solutions (25 ml each) were heated to 60°C, and the pH of the solutions was adjusted to 4.0–5.0, if necessary, with dilute acetic acid. Thiourea (^{13}C labeled) was then added and allowed to mix for a few minutes with the solution during stirring. A portion of the solutions was quickly transferred to an NMR tube and immediately spun for 2–4 minutes in a controlled 60°C temperature environment to accumulate enough data for a sufficient signal, while the pH of the rest of the solutions was adjusted to 6.8–7.2 with ammonia. ^{13}C spectra of these solutions were run in turn, keeping the spinning times the same. The time span between the start of the reaction and the end of the NMR runs was 10–15 minutes for each experiment.

We also investigated the reaction of thiourea with hydrogen peroxide at 60°C at pH < 1. Initially, the pH of the stock hydrogen peroxide solution was set to <1 with dilute hydrochloric acid prior to thiourea addition, and then the required amount of thiourea was added and the ^{13}C NMR of a part of the reaction mixture run as before, while the pH of the rest of the mixture was adjusted to 6.8–7.2 with aqueous ammonia. This was in turn run to permit monitoring of different species that form and decompose under such conditions. Thus, we could study the stability of the reaction products at a given concentration of reactants, pH of the medium, and temperature over a prolonged time period. Hydrogen peroxide concentration was increased in small increments to allow detection of the intermediates before their decomposition. We also investigated the reaction of thiourea with hydrogen peroxide at 60°C under neutral conditions, where the pH of the reaction was kept at 7.0–7.2 throughout by using a strong buffer mixture (KH_2PO_4/NaOH).

Individual ^{13}C NMR spectra of thiourea (^{13}C labeled) and of each of its possible reaction products with hydrogen peroxide (thiourea dioxide, formamidine disulfide dihydrochloride, and urea) were run at different pH values (<1, 4.5, and 7.1). High concentrations (20 g/l) of reagents were used in the case of unlabeled compounds to overcome the weakness of

the signal arising from the low abundance of ^{13}C in naturally occurring carbon.

Results and Discussion

For ^{13}C NMR spectroscopy to be a useful tool for studying these chemical reactions, we had to collect sufficient data in a short time span to yield an adequate signal, since reaction intermediates might form and then decompose. Preliminary experiments showed that an adequate signal may be obtained in a matter of minutes using ^{13}C-labeled thiourea as the reactant. Since there is no other carbon atom involved in the reaction, all carbon-containing products are likewise ^{13}C labeled, and reaction products appear to be clearly resolved and assignable.

The ^{13}C NMR spectra of thiourea (^{13}C labeled), thiourea dioxide, formamidine disulfide dihydrochloride, and urea were individually taken in aqueous solutions of different pH values. The ^{13}C shifts of individual compounds are shown in Table I; they agree closely with the findings of Kelner *et al.* [15] and are clearly resolved from one another. Having obtained the individual ^{13}C NMR signals for each reagent, we were able to run the reaction under bleaching conditions to identify qualitatively what was being formed. We observed the same reaction intermediates and products from hydrogen peroxide and thiourea under bleaching conditions, regardless of whether tetrasodium pyrophosphate or Prestogen NB-W was present in solution as alkaline stabilizer or acidic activator for hydrogen peroxide, respectively. In both cases the pH of the solution was adjusted to 4.0–5.0, if necessary, before thiourea addition.

The results of such ^{13}C NMR runs are shown in Table I for various molar ratios of the reactants. Typical ^{13}C spectra of some of the runs are also shown in Figure 2. In run 5, the quantity of thiourea was well in excess of that of hydrogen peroxide in the reaction mixture (the $[H_2O_2]:[Th]$ ratio would be 2.0 for conversion of thiourea to thiourea dioxide). As a result, the reaction (pH = 4.5, 60°C) yielded a mixture of thiourea and thiourea dioxide (Figure 2a), which are distinctly separable as shown. On pH adjustment to 7.1, even though we observed a rapid surge in redox potential to a negative value, there was only the slightest indication of the formation of the hydrolysis product, urea (Figure 2b). However, there were changes in the relative sizes of the thiourea and thiourea dioxide peaks. It only takes a very small amount of the other product of thiourea dioxide hydrolysis, sulfinate anion, to generate such a highly negative redox potential, since sulfinate is a strong reducing agent.

TABLE I. ^{13}C chemical shifts (ppm) of reactants, intermediates and products of the reaction between thiourea and hydrogen peroxide at various pH values at 60°C.[a]

Run number, reagent(s)	pH	Th	ThDO	FDS	Urea	NC-NH_2	Redox potential, mV
1 Thiourea (Th)	1.0	184.5	–	–	–	–	+173
	4.5	184.5	–	–	–	–	–
	7.1	184.5	–	–	–	–	−70
2 Thiourea dioxide (ThDO)[b]	4.5	–	179.8	–	–	–	−380
	7.1	–	179.8	–	165.5	–	−744
3 Formamidine disulfide (FDS)[b,c]	<1.0	–	–	169.8	–	–	–
	7.1	184.1	–	–	–	120.9	−120
4 Urea[b]	4.5	–	–	–	164.7	–	–
	7.1	–	–	–	164.7	–	–
5 $[H_2O_2]:[Th] = 1.1$	4.5	183.9	179.5	–	–	–	+191
	7.1	183.9	179.5	–	–	–	−637
6 $[H_2O_2]:[Th] = 2.0$	4.5	–	180.5	–	–	–	+186
	7.1	–	180.5	–	–	–	−637
7 $[H_2O_2]:[Th] = 3.2$	4.5	–	179.8	–	165.5 (s)	–	+258
	7.1	–	–	–	165.5	–	−630
8 $[H_2O_2]:[Th] = 4.4$	4.5	–	179.5	–	164.7 (m)	–	+290
	7.1	–	–	–	164.7	–	+210
9 $[H_2O_2]:[Th] = 0.74$	<1.0	–	–	169.8	–	–	+376
	7.1	184.5	–	–	–	120.9	−120
10 $[H_2O_2]:[Th] = 3.2$	<1.0	–	180.2 (m)	168.9	–	–	–
	7.1	–	–	–	164.9	120.2 (m)	+70
11 $[H_2O_2]:[Th] = 2.0$	7.1	184.8 (m)	–	–	165.5	–	−200
12 $[H_2O_2]:[Th] = 3.2$	7.1	184.5 (t)	180.2 (t)	–	164.8	120.2 (t)	−152

[a] Th = thiourea, ThDO = thiourea dioxide, FDS = formamidine disulfide, NC-NH_2 = cyanamide, (t) = trace peak, (s) = small peak, (m) = medium peak. [b] High concentration (20 g/l) and low temperature (21°C) were used to accumulate sufficient data in 2–4 hours for the nonlabeled reagents. [c] Dihydrochloride salt is used as bought.

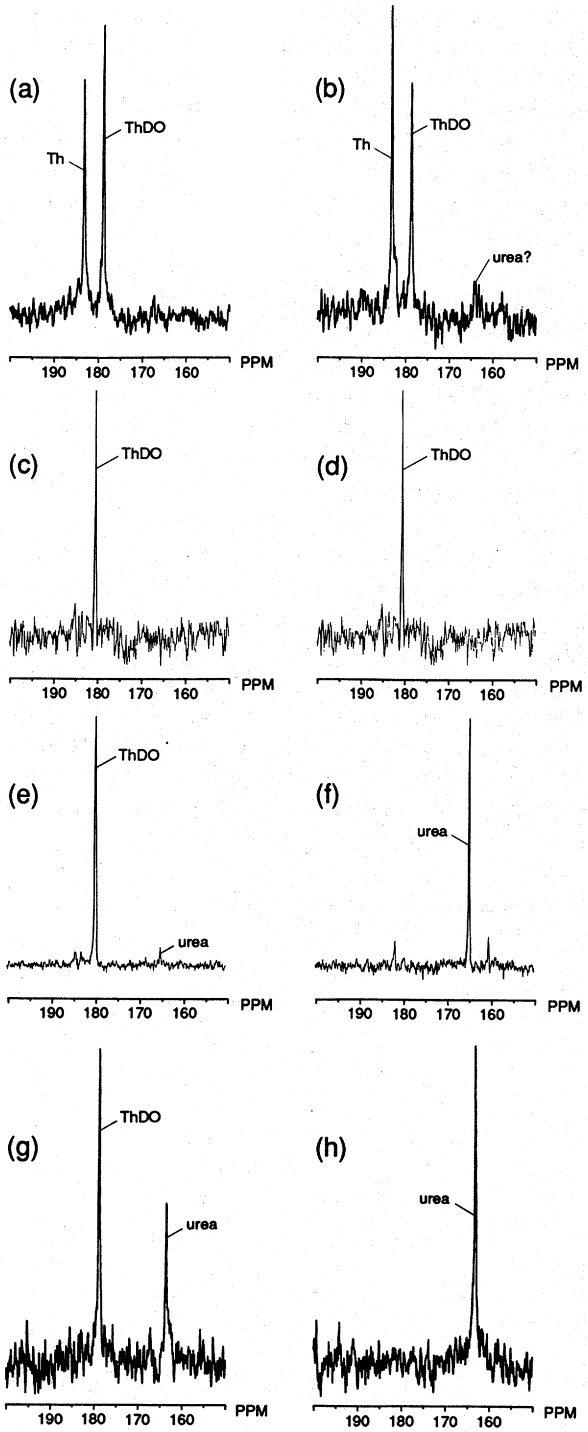

FIGURE 2. ^{13}C NMR spectra of products of reactions between hydrogen peroxide and thiourea; abbreviations as per Table I: (a) $[H_2O_2]:[Th] = 1.1$ (Table I, run 5, $pH_i = 4.5$), (b) a after pH adjustment to 7.1, (c) $[H_2O_2]:[Th] = 2.0$ (Table I, run 6, $pH_i = 4.5$), (d) c after pH adjustment to 7.1, (e) $[H_2O_2]:[Th] = 3.2$ (Table I, run 7, $pH_i = 4.5$), (f) e after pH adjustment to 7.1, (g) $[H_2O_2]:[Th] = 4.4$ (Table I, run 8, $pH_i = 4.5$), (h) g after pH adjustment to 7.1.

In run 6, stoichiometric amounts of thiourea and hydrogen peroxide were mixed together; the NMR spectrum shows only thiourea dioxide (Figure 2c). On pH adjustment, we saw no change in the NMR spectrum (Figure 2d), but a highly negative redox potential suggests some hydrolysis.

In run 7, the quantity of hydrogen peroxide was in excess of that required to convert the thiourea to thiourea dioxide, and as a result, the reaction (pH = 4.5, 60°C) yielded a major signal for thiourea dioxide with a much smaller signal for urea, even at pH = 4.5 (Figure 2e). On pH adjustment to 7.1, there was a rapid surge in redox potential to a highly negative value (−630 mV) with a complete hydrolysis of thiourea dioxide to urea and sulfinate anion (Figure 2f). Even though thiourea is converted to thiourea dioxide, there is still excess hydrogen peroxide remaining in the reaction mixture; that excess reacts with thiourea dioxide, converting some of it to sulfate anion and urea until all hydrogen peroxide is consumed. Overall, sulfinate anion species dominate in solution, giving rise to a high negative redox potential. We recommend this molar ratio of reactants as the most efficient, most economical, and safest for the reductive step of our dual bleaching process [1–3]. Less thiourea is needed in proportion to the amount of residual hydrogen peroxide remaining from the earlier oxidative bleaching step. Complete consumption of toxic thiourea is assured. Thiourea dioxide, when hydrolyzed, is such a strong, stable reductive bleach that above a certain concentration the bleaching effectiveness stays virtually unchanged [7].

On the other hand, when too little thiourea is added (run 8), hydrogen peroxide appears to enhance the decomposition of thiourea dioxide as the latter forms. The presence of urea even at pH = 4.5 was very apparent (Figure 2g), and the positive redox potential indicates that any reductive sulfinate ion is oxidized by the preponderance of hydrogen peroxide. Any remaining thiourea dioxide is destroyed rapidly on adjusting the pH to 7.1 (Figure 2h), and the redox potential remains positive.

The products of the reaction of thiourea with hydrogen peroxide initiated at pH < 1 at 60°C were dependent on the molar ratio of reactants and differed from the products of reactions initiated at pH = 4.5. Formamidine disulfide dihydrochloride is the major product of the reaction between thiourea and hydrogen peroxide in the presence of hydrochloric acid (pH < 1). Formamidine disulfide dihydrochloride decomposes rapidly in aqueous solutions at pH > 1. The higher the pH the faster the rate of decomposition. The disulfide

does decompose, however, in aqueous solutions at pH < 1, albeit over a long period of time. The rate of decomposition is even further accelerated by heat. Formamidine disulfide decomposes rapidly on heating and at pH values > 1 to thiourea, cyanamide, and colloidal sulfur. We also observed these species in run 9, where a mole of thiourea was brought into contact with 0.74 mole of hydrogen peroxide in hydrochloric acid (pH < 1). There was a single ^{13}C signal at pH < 1, corresponding to formamidine disulfide. On pH adjustment to 7.1, formamidine disulfide rapidly decomposed (even faster at a high temperature) to thiourea, cyanamide, and colloidal sulfur. We believe that the weak redox potential (−120 mV) is due to the presence of thiourea, which is weakly reductive under these conditions.

For a greater molar ratio of hydrogen peroxide to thiourea (3.2, run 10), formamidine disulfide was the main product formed at pH < 1. Since there was excess hydrogen peroxide remaining in the reaction, however, various oxidation products of formamidine disulfide were formed and decomposed until all the hydrogen peroxide was consumed. On pH adjustment to 7.1, urea and cyanamide were formed and the redox potential remained positive. Since most of the oxidation products of disulfides are easily decomposed at neutral and alkaline pH, there may have been many oxidation products formed in the reaction prior to pH adjustment to 7.1, but owing to rapid decomposition they were not easily observed.

To clarify this point, we added small amounts of hydrogen peroxide to a given solution of thiourea set at pH < 1 and observed the stabilities of the reaction products over a longer period of time by scanning the mixture twice in succession. It is clear that formamidine disulfide was the main reaction product for $[H_2O_2]$: [thiourea] = 0.74 at 60°C. When we scanned the solution again after 10 minutes, however, we saw a small signal due to cyanamide. This may be because a small amount of hydrogen peroxide may have reacted with formamidine disulfide to yield cyanamide [12].

We then added more hydrogen peroxide to the reaction mixture (still at pH < 1 at 60°C), making the ratio $[H_2O_2]$: [thiourea] = 2.0. Owing to the formation of various intermediates, a longer scanning time (100 scans) was needed to be able to see the intermediate species because their concentration in the reaction mixture was rather small. On first scanning, we saw a major signal at δ = 180.69 ppm, a medium multiplet signal at around δ = 170.0 ppm, a medium urea signal at δ = 165.34 ppm, and a medium cyanamide signal at δ = 120.70 ppm. On second scanning (146 scans), we saw the same signals as above except that the relative sizes of the peaks in the multiplet signal seemed to have changed. The signal at δ = 180.69 ppm may either be due to thiourea dioxide or the oxidation products (monoxide and dioxide) of formamidine disulfide, the carbon observed being adjacent to the oxidized S atom. The multiplet at around δ = 170.0 ppm is partly due to the disulfide and partly to the incompletely oxidized disulfide's carbon atom adjacent to the non-oxidized sulfur atom.

We then added even more hydrogen peroxide to the reaction mixture, still at pH < 1 and 60°C, making the ratio $[H_2O_2]$: [thiourea] = 3.2. On first scan (100 scans), we observed signals similar to those noted above, except that the relative sizes of the peaks were altered and the multiplet at around δ = 170.0 ppm seemed to be gradually disappearing, while a urea signal at δ = 165.44 ppm emerged as the predominant peak. On second scan (71 scans), the multiplet signal had disappeared while the other signals were still there. On pH adjustment of the reaction mixture to 7.1 and additional scanning (100 scans), only two peaks (a major urea signal and a minor cyanamide signal) remained, the redox potential being positive throughout the reaction sequence. We therefore think that the signal at δ = 180.69 ppm is due to the intermediate oxidation products of formamidine disulfide and not thiourea dioxide. This is supported by the redox potentials. Had thiourea dioxide formed, then on hydrolysis at pH = 7.1, we should have seen a rapid surge in redox potential to a high negative value (−630 mV) as in run 7. Since a positive redox potential was maintained throughout the reaction, the intermediate oxidation products of formamidine disulfide likely formed and then on pH adjustment to 7.1 at 60°C were unstable and easily hydrolyzed to urea and sulfate anion.

The buffered (pH = 7.1) reaction of thiourea with hydrogen peroxide at different molar ratios at 60°C is thought to proceed by means of the direct oxidation of thiourea to formamidinesulfenic acid (Figure 1), then formamidinesulfinic acid (thiourea dioxide), and eventually to urea and sulfate anion. For $[H_2O_2]$: [thiourea] = 2.0 (run 11), we observed two distinct signals due to thiourea and urea with a small negative redox potential. Even though we scanned the reaction mixture within 10 minutes, we saw none of the intermediate reaction products. We think this is because as the intermediates are formed, they are instantly hydrolyzed in solution (pH = 7.1) at 60°C, giving rise to highly reductive products (sulfenate and sulfinate anions). Since these are much stronger reducing agents than thiourea, they are oxidized first to the sulfate anion

before hydrogen peroxide can react with more thiourea. Some thiourea remains unreacted, because all the hydrogen peroxide is consumed by the other highly reductive species. However, when more hydrogen peroxide is present in the reaction medium, as is the case in run 12, then there is a major signal due to urea with trace amounts of thiourea, thiourea dioxide, and cyanamide. Here there is a sufficient amount of hydrogen peroxide to react with almost all of the thiourea, and all sulfur-containing species convert to sulfate anion and urea.

Only under strongly acidic conditions (mineral acid, pH < 1) does thiourea behave like a true thiol by undergoing oxidation to the disulfide species [4, 25]. In slightly acidic and neutral media, on the other hand, the direct oxidation of the S atom to sulfenate, sulfinate, and eventually sulfate species is the likely route, as evident from ^{13}C NMR spectroscopy.

Conclusions

The reaction route and the final products of the reaction of thiourea with hydrogen peroxide depend very much on the molar ratio of reactants and the pH of the reaction. The reaction rate on the other hand is accelerated by increasing the temperature (60°C in our experiments), though the reaction is reasonably fast and exothermic even at ambient temperatures. If it takes place in a strongly acidic (pH < 1) medium, the reaction proceeds by means of the disulfide intermediate. Numerous intermediates and products are possible, depending on the molar ratio of reactants and the timing of the pH adjustment to 7.1. Under slightly acidic (pH = 4.5) and neutral pH, the reaction of thiourea with hydrogen peroxide proceeds by means of the direct oxidation of the sulfur atom of thiourea, giving rise to formamidinesulfenic acid, formamidinesulfinic acid (thiourea dioxide), and finally sulfate anion and urea. Again, the reaction intermediates and products depend very much on the molar ratio of reactants as well as the temperature and the timing of the pH adjustment. The reaction of thiourea with hydrogen peroxide is interesting because one of the reaction products (thiourea dioxide) is used as a reductive bleaching agent for textile fibers. Under the oxidative bleaching conditions at 60°C in our dual bleaching process [1–3], it is essential that the reaction of thiourea with hydrogen peroxide be run under slightly acidic conditions (pH 4.0–5.0) for at least 10 minutes before the pH of the medium is adjusted to 6.5–7.0. In this way, all the thiourea is converted to thiourea dioxide. Premature pH adjustment of the reaction medium to 6.5–7.0 at 60°C causes rapid hydrolysis of thiourea dioxide as it forms. Sulfinate anions then compete with thiourea for the remaining hydrogen peroxide, and the former reaction is very much favored over the latter owing to the stronger reducing properties of the sulfinate anions. As long as the pH of the reaction medium is kept slightly acid (pH 4.0–5.0) while the reaction is taking place, hydrogen peroxide will react preferentially with thiourea over thiourea dioxide, because under such pH conditions thiourea dioxide is not hydrolyzed to a great extent and hence is less of a reducing agent [11, 26] than thiourea. Therefore, thiourea is favored over thiourea dioxide for reaction with hydrogen peroxide. Once thiourea is converted to thiourea dioxide, pH adjustment to 7.1 causes hydrolysis to the highly reductive sulfinate ion, and reductive bleaching can occur.

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