Full Paper

Oxyhalogen–Sulfur Chemistry: Oxidation of a Thiourea Dimer, Formamidine Disulfide, by Chlorine Dioxide

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The oxidation of formamidine disulfide, FDS, the dimer of thiourea, by aqueous chlorine dioxide has been studied in highly acidic and mildly acidic media. FDS is one of the possible oxidation intermediates formed in the oxidation of thiourea by oxyhalogens to urea and sulfate. The reaction is exceedingly slow, giving urea and sulfate with a stoichiometric ratio of 5 : 14 FDS to chlorine dioxide after an incubation period of up to 72 h and only in highly acidic media which discourages the disproportionation of chlorine dioxide to the oxidatively inert chlorate. Mass spectrometric data suggest that the oxidative pathway proceeds predominantly through the sulfinic acid, proceeding next to the products sulfate and urea, while by-passing the sulfonic acid. Transient formation of the unstable sulfenic acid was also not observed.

Introduction

Reactions of oxyhalogens and organosulfur compounds are invariably complex. The complexities arise from both the sulfur and oxyhalogen chemistries. The first chemical oscillators; the Belousov–Zhabotinski (BZ),[1,2] Bray–Liebhafsky (BL),[3,4] and Briggs Rauscher (BR)[5–8]reactions were all derived from oxyhalogen chemistry. The underlying mechanism in all of them involves an autocatalytic feedback loop.[9] This autocatalysis gives the chemical system the necessary complexity to generate oscillatory behaviour. Sulfur's complexities arise from generation of free-radical mechanisms, autoxidations, and the propensity to form sulfur–sulfur bonds leading to various polymeric sulfur species.

During the systematic design of chemical oscillators, it was noticed that oxidation of a sulfur compound can yield oscillatory behaviour in a continuously-stirred tank reaction (CSTR), and display clock[10] and crazy clock reaction characteristics, stirring rate effects, chemical chaos,[11–14] travelling waves,[15] and gravity-induced anisotropies in travelling and spatiotemporal patterns.[16] The reaction combination of oxyhalogens (chlorite,[17] iodate, bromate, and bromite) with organosulfur compounds is a rich source for the generation of exotic dynamics. None of these oxyhalogen–organosulfur oscillators have been as completely characterised as the BZ reaction. The derivation of the mechanistic basis of oscillatory behaviour depends on the evaluation of the kinetics and mechanisms of the 25 or more reactions that are viable in the reaction mixture.

We recently attempted to derive a general mechanism for oxyhalogen–organosulfur interactions by using oxychlorines and thioureas as the base reactants. In this case we attempted to work with the chlorite–thiourea reaction. Using previously

gathered information and our own intuition, we came up with a comprehensive reaction scheme that could include all possible feasible reactions in this reaction system. This enabled us to study individual reactions in isolation, deriving the attendant kinetics and mechanisms of each, and then combining them all to produce the comprehensive reaction scheme whose veracity can then be evaluated through complementary modelling techniques. The comprehensive reaction scheme is shown in Scheme 1.

Generally, the global kinetics of this reaction scheme are controlled by the formation and consumption of HOCl, which is known to be the autocatalytic species in chlorite oxidations, just as HBrO₂ acts in the same manner for bromate oxidations.[18] In acidic media, chlorite oxidations proceed in two-electron steps, with the initial step yielding HOCl:[19]

$$ClO_2^- + 3H^+ + 2e^- \rightarrow HOCl + H_2O \qquad (1)$$

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (2)$$

In excess chlorite, HOCl will be produced autocatalytically through the well known asymmetric intermediate, Cl₂O₂:[19]

$$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O \qquad (3)$$

$$Cl_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2HOCl \qquad (4)$$
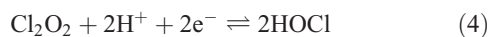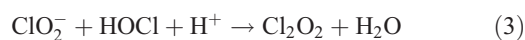
A combination of Reactions 3 and 4 in tandem shows quadratic autocatalysis where one mole of HOCl gives two moles of the same as the reaction proceeds. If oxidation rates by

Scheme 1.

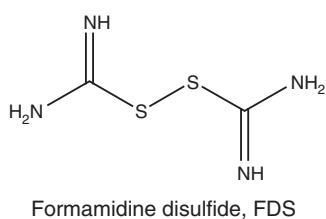

Formamidine disulfide, FDS
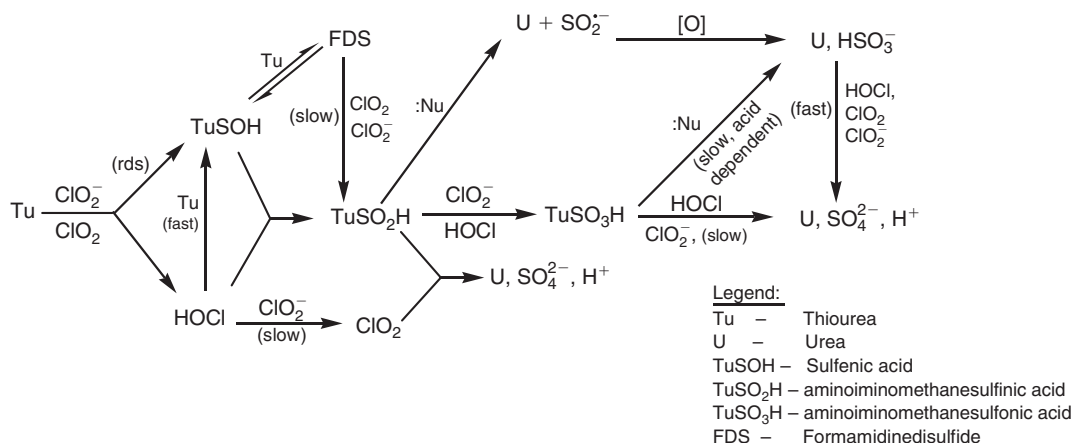
Chart 1.

HOCl are faster than those by chlorite, then the reaction will proceed autocatalytically.

The presence of HOCl brings to the fore a new reaction and a new oxidant; ClO_2:[20]

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2(aq) + Cl^- + H_2O \qquad (5)$$

The fate of chlorine dioxide is dependent on the rate of its reaction with the organosulfur compounds. If these rates are rapid and much faster than that of Reaction 5, chlorine dioxide will not be observed in the reaction medium, and if it is, it would mean that all organosulfur species have been depleted. Previous work from our laboratory has shown that oxidation rates by chlorine dioxide are comparable to those by HOCl. This sometimes results in transient chlorine dioxide formation, even though the overall stoichiometry does not involve chlorine dioxide as a final product. This was initially observed, in our laboratories, in the oxidation of phenylthiourea by chlorite.[21]

On the organosulfur chemistry side, there are several oxidation products that can be formed before formation of sulfate. The major products of oxidation are the sulfinic and sulfonic acids and the dimeric species. Sulfenic acids have always been considered to be too reactive to be isolated, except in sterically hindered analogues.[22,23] Reactions of the sulfinic acid of thiourea with chlorite have been studied[24] as well as its decomposition.[25,26] One major oxidation product which has so far been ignored is the dimer, formamidine disulfide (FDS) (Chart 1). In excess reductant, it would be the dominant oxidation product. It is manufactured on commercial levels by air oxidation of thiourea or by the use of limited amounts of hydrogen peroxide. Due to the bulkiness of the groups surrounding the thiocarbonyl bond, polymerization does not proceed past the dimer.

Here we report on the oxidation of FDS by chlorine dioxide. This study will help in deriving mechanistic details of a very important reaction in the oxidation by chlorite of thiourea (see Scheme 1).

Experimental

Materials

The following reagents were used without further purification: formamidine disulfide dihydrochloride (FDS, 97 %), soluble starch, sodium thiosulfate, sodium chlorate, perchloric acid (70 %), hydrochloric acid, oxalic acid, sulfuric acid (Fisher), and thiourea (TU, 99 % Lancaster). Sodium chlorite (Fisher) was recrystallised from a water/methanol/ethanol mixture to give a purity greater than 95 %. Chlorine dioxide was prepared by reducing sodium chlorate in a sulfuric/oxalic acid mixture and then stored in perchloric acid at 4°C.[27] The recrystallised chlorite and chlorine dioxide solutions were standardised iodometrically by adding excess acidified iodide to the solution with the released iodine titrated against standard thiosulfate. Stock solutions of FDS were prepared in excess perchloric acid to minimise decomposition and were not kept for more than 1 h. Distilled deionised water was used for the preparation of all stock solutions.

Methods

All experiments were carried out at 25 ± 0.1°C and the solutions were made to a constant ionic strength of 1.0 M with $NaClO_4$. All kinetics measurements were performed on a Hi-Tech Scientific SF-61 AF single mixing stopped-flow spectrophotometer. Reaction progress was followed by monitoring the formation and disappearance of chlorine dioxide at 360 nm (absorptivity coefficient 1265 M^{-1} cm^{-1}).

Time-of-Flight Mass Spectrometry

Mass spectra were acquired on a Micromass QTOF-II (Waters Corporation, Millford, MA) quadrupole time-of-flight mass spectrometer (QTOF MS). Analytes were dissolved in a 50/50 (v/v) acetonitrile/water–1 % formic acid mixture, and analyte ions were generated by positive-mode electrospray ionisation (ESI) at a capillary voltage of 2.8 kV and a flow rate of 5 μL min^{-1}. The source block was maintained at 80°C and the nitrogen desolvation gas was maintained at 150°C and a flow rate of 400 L h^{-1}. For each reaction solution, a control
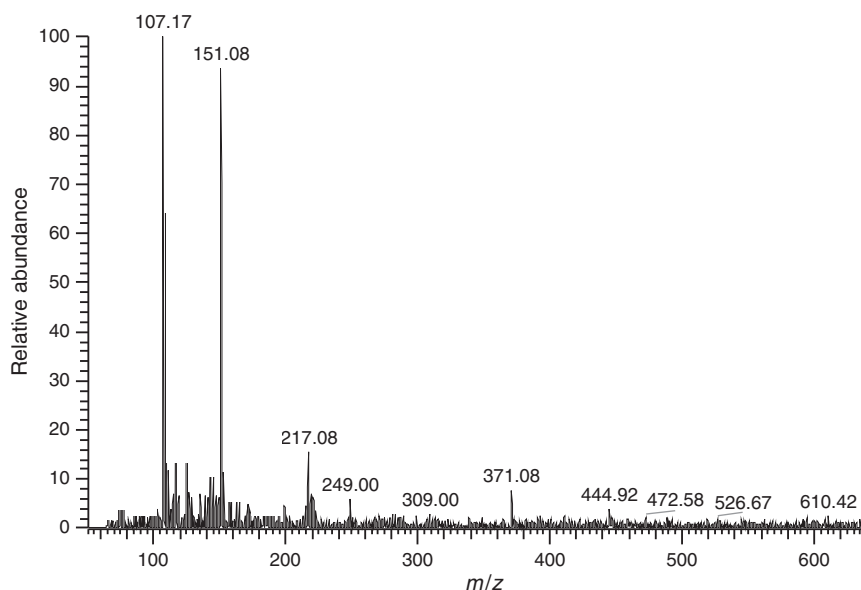
Fig. 1. Positive mode electrospray ionisation mass spectrum for the formamidine disulfide (FDS)–chlorine dioxide reaction in high excess of oxidant taken 2 min after reaction initiation. Apart from the peak denoting the substrate, FDS at *m/z* 151; the sulfinic acid also shows up in high abundance at *m/z* 107.

experiment was performed in which all conditions were matched except for the oxidant. This is necessary for unambiguous mass spectral data interpretation. Data were visualised and analysed with the Micromass MassLynx 4.0 software suite for Windows XP (Waters Corporation, Millford, MA).

Stoichiometric Determinations

The stoichiometric determinations involving chlorine dioxide reactions were done at fixed substrate concentrations in excess chlorine dioxide, with the depletion of chlorine dioxide, after prolonged standing, taken as the stoichiometric equivalent to substrate concentration. The solutions were first kept in the dark for 24 h and the chlorine dioxide remaining quantified using iodometric and spectrophotometric techniques (at 360 nm). One complicating reaction was the general disproportionation of chlorite solutions on prolonged standing:[28]

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2(aq) + Cl^- + 2H_2O \qquad (6)$$
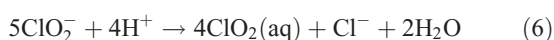
Chlorite was a possible intermediate reduction species, especially in excess oxidant. While Reaction 6 distorted spectrophotometric determinations; it retained the oxidising power invariantly. Thus, iodometric techniques still applied, despite the disproportionation.

Results

The chlorine dioxide–FDS reaction was exceedingly slow, such that, even after 48 h, the reaction had not gone to completion with approximately equimolar concentrations of FDS and ClO_2. The oxidation of thiourea gives one unstable (sulfinic acid) and three stable oxidation intermediates (disulfide, dioxide, and trioxide) before formation of the final oxidation products (sulfate and urea). The stable intermediates are oxidized further at an extremely slow rate. FDS appears to be the most stable and unreactive of all the oxidation intermediates studied so far. The reaction stoichiometry was elusive and could only be
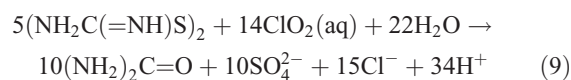
determined in excess oxidant and after prolonged incubation of over 72 h. Initially, in this study, the stoichiometry of the chlorite–FDS reaction was deduced by titrimetric techniques in excess oxidant conditions, in which a 2 : 7 ratio was deduced:

$$2NH_2C(=NH)S)_2 + 7ClO_2^- + 6H_2O \rightarrow$$
$$4(NH_2)_2C=O + 4SO_4^{2-} + 7Cl^- + 8H^+ \qquad (7)$$
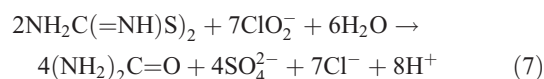
All the sulfur was quantitatively obtained as sulfate. In a previous study from this laboratory,[29] the stoichiometry of the oxidation of a substituted thiourea (*N*-acetylthiourea) by chlorine dioxide was deduced as:

$$8ClO_2(aq) + 5CH_3C(=O)NHC(NH_2)=S + 9H_2O \rightarrow$$
$$5CH_3C(=O)NH(NH_2)=O + 5SO_4^{2-} + 8Cl^- + 18H^+ \quad (8)$$
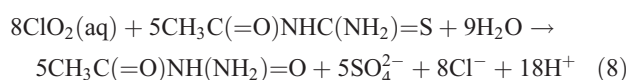
The expected stoichiometry of the FDS–ClO_2 reaction is:

$$5(NH_2C(=NH)S)_2 + 14ClO_2(aq) + 22H_2O \rightarrow$$
$$10(NH_2)_2C=O + 10SO_4^{2-} + 15Cl^- + 34H^+ \qquad (9)$$

Titrimetric determinations, however, overestimated the amount of ClO_2 needed because, in low acid concentrations, and on prolonged standing, instead of disproportionating according to Reaction 6, some of the chlorine dioxide disproportionates into inert ClO_3^- which did not contribute to the titer.[30]

Product Analysis

Mass spectral data showed a very complex reaction. The reaction showed variable intermediates and products depending on the concentration of oxidant relative to the reductant. The reaction was easier to interpret in overwhelming excess of oxidant. Fig. 1 shows the mass spectrum obtained at the
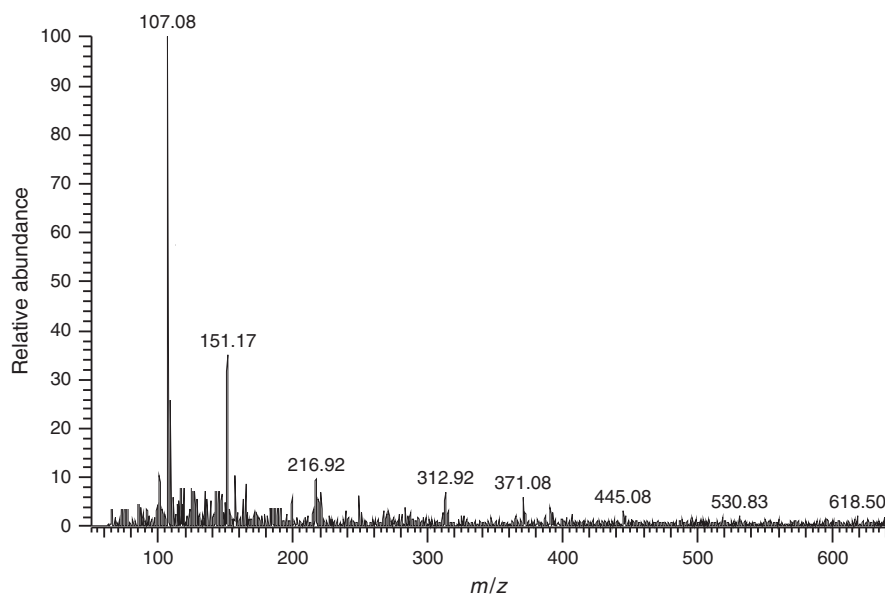
Fig. 2. Positive mode mass spectrum for the reaction solution in Fig. 1 taken at 5 min from initiation. Here, the substrate peak decreases as expected and the sulfinic acid peak strengthens. At this point, not much of the product, urea, has been formed.
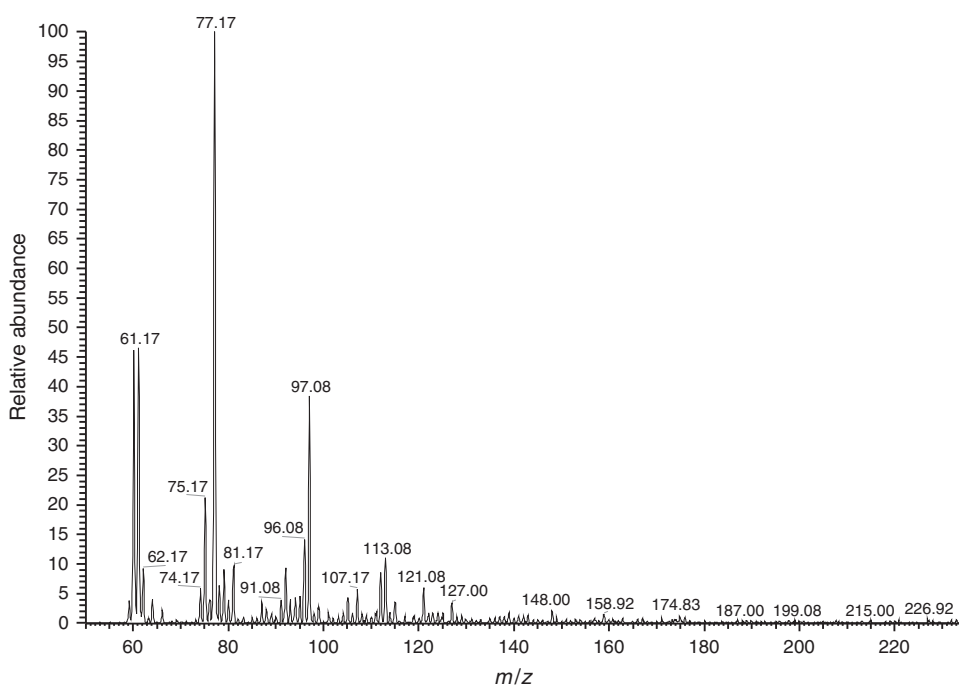

Fig. 3. Negative mode electrospray ionisation mass spectrum, taken after 24 h, for the formamidine disulfide (FDS)–chlorine dioxide reaction in approximately equimolar concentration ratios of oxidant to reductant. The spectrum shows that the initial step for the oxidation of FDS is through the initial formation of thiourea and the sulfenic acid (Reaction 10). The thiourea peak is quite visible (*m/z* 77). The sulfenic peak is not detected due to its instability. The products urea (*m/z* 61) and sulfuric acid (*m/z* 97) are also evident. Very little sulfinic acid is detected under these conditions after 24 h.

beginning of the reaction (2 min). It shows a strong and visible peak for the substrate (FDS) at *m/z* 151 and an equally strong peak for the sulfinic acid (aminoiminomethanesulfinic acid, AIMSA, thiourea dioxide) at *m/z* 107. At 5 min, the FDS peak starts to decrease, while the AIMSA peak becomes more dominant, relative to FDS (Fig. 2). After incubation periods of 72 h, the peak for FDS completely disappears and the spectrum shows

a strong peak for urea, the oxidation product. Fig. 3 shows the mass spectrum obtained after an incubation period of 24 h at excess reductant concentrations (negative mode). Very little AIMSA is obtained after this incubation period. Instead, urea and thiourea are obtained (*m/z* 61 and 77, respectively). Acid was also important in determining the abundance of intermediates. Highly acidic environments encouraged formation
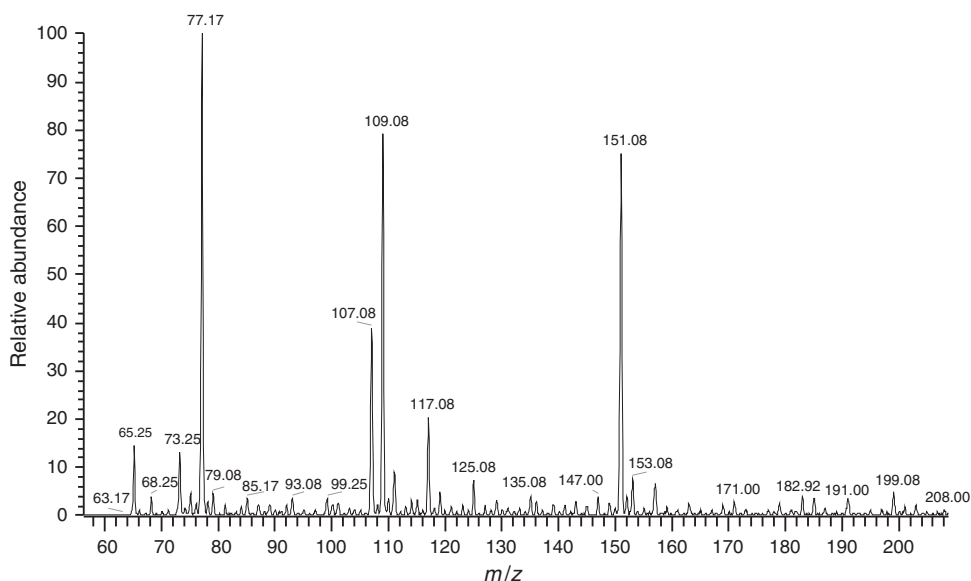
Fig. 4. Comparative spectrum: thiourea–chlorine dioxide reaction in excess oxidant after 2 min. One of the major intermediates at this early stage of the reaction is the dimer, formamidine disulfide (FDS) (*m/z* 151). The other intermediate is the sulfinic acid (*m/z* 109 and 107). Very little sulfonic acid at *m/z* 125 is formed.
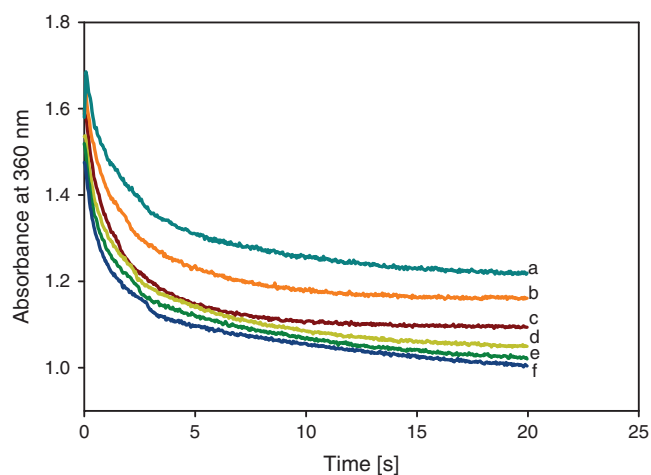

Fig. 5. Effect of acid on the formamidine disulfide (FDS)–chlorine dioxide reaction. $[FDS]_0 = 1.0 \times 10^{-3}$ M; $[ClO_2]_0 = 1.2 \times 10^{-3}$ M. $[H^+]_0 = 0.01$ (a), 0.02 (b), 0.03 (c), 0.04 (d), 0.05 (e), and 0.06 M (f).
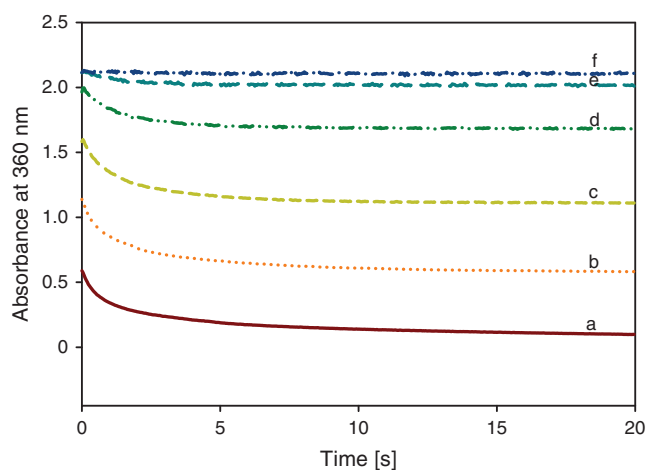

Fig. 6. Effect of the variation of chlorine dioxide on the formamidine disulfide (FDS)–chlorine dioxide reaction in acidic medium. $[FDS]_0 = 1.0 \times 10^{-3}$ M; $[H^+]_0 = 0.01$ M. $[ClO_2]_0 = 5.0 \times 10^{-4}$ (a), 1.0×10^{-3} (b), 1.5×10^{-3} (c), 2.0×10^{-3} (d), 2.5×10^{-3} (e), and 3.0×10^{-3} M (f).

and stabilisation of AIMSA, while weakly acidic conditions destabilised the sulfinic acid and product formation while giving larger peaks for thiourea. In contrast, Fig. 4 shows the mass spectrum of the thiourea–chlorine dioxide reaction after 2 min. This spectrum was taken in excess chlorine dioxide over thiourea. This reaction is much faster than the FDS analogue. It shows peaks for the substrate thiourea and FDS. It also shows peaks for AIMSA (*m/z* 109 and 107) as well as the product urea. This spectrum shows that the dimeric species is a viable intermediate in any oxidation of thiourea, and that its further oxidation is an important component reaction in the overall reaction scheme of the oxidation of thiourea.

Reaction Kinetics

The reaction showed an initial rapid rate, followed by a gradual slowing down as the reaction proceeds. This is typical of

bimolecular kinetics and auto-inhibitory dynamics. Fig. 5 shows that the reaction is catalysed by acid. Due to its complexity, there was no simple relationship that could be derived from the experimental data linking rate with acid concentrations. Two series of reactions were undertaken: one in the presence of acid, and another without added acid. Due to the stability of chlorine dioxide in acidic media, reactions run in acid were more reproducible, and thus all reaction kinetics profiled in this report were run under acidic conditions. Fig. 6 shows the effect of chlorine dioxide on the rate of reaction in 0.01 M acid. The kinetics profile also shows the initial rapid step followed by slow consumption of chlorine dioxide. The rate of consumption of chlorine dioxide, in the rapid initial stage, followed first order kinetics with respect to chlorine dioxide. Fig. 7 shows the effect of FDS concentration and Fig. 8 shows that this effect is first order.
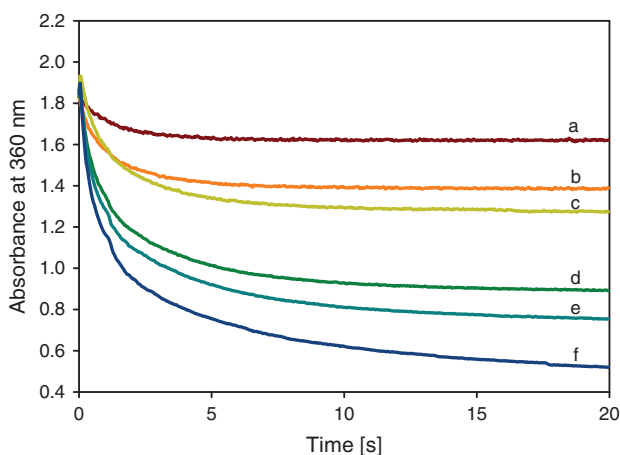
Fig. 7. Effect of the variation of formamidine disulfide (FDS) on the FDS–chlorine dioxide reaction in acidic medium. $[ClO_2]_0 = 1.0 \times 10^{-3}$ M; $[H^+]_0 = 0.01$ M. $[FDS]_0 = 5.0 \times 10^{-4}$ (a), 1.0×10^{-3} (b), 1.5×10^{-3} (c), 2.0×10^{-3} (d), 2.5×10^{-3} (e), and 3.0×10^{-3} M (f).
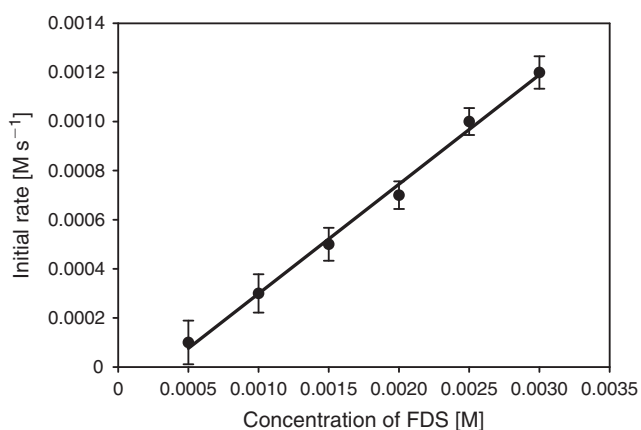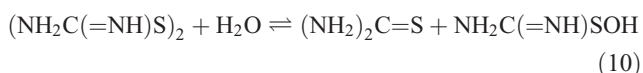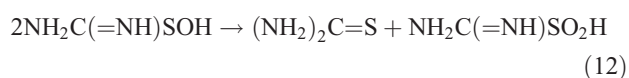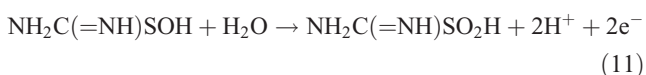

Fig. 8. Initial rate plot for the variation of formamidine disulfide (FDS) in 0.01 M acid (data from Fig. 7). The linear plot suggests that the reaction is first order in FDS.

Mechanism

Mass spectrometric data analysis shows that the initial step is the hydrolysis of FDS into the unstable sulfenic acid and thiourea:

$$(NH_2C(=NH)S)_2 + H_2O \rightleftharpoons (NH_2)_2C=S + NH_2C(=NH)SOH \tag{10}$$

The sulfenic acid is highly reactive and will be rapidly oxidised to the sulfinic acid or disproportionate into thiourea and sulfinic acid.

$$NH_2C(=NH)SOH + H_2O \rightarrow NH_2C(=NH)SO_2H + 2H^+ + 2e^- \tag{11}$$

$$2NH_2C(=NH)SOH \rightarrow (NH_2)_2C=S + NH_2C(=NH)SO_2H \tag{12}$$

The disproportionation reaction (Reaction 12) is the dominant pathway in conditions of excess reductant such that addition of four oxidation equivalents will halt the oxidation of thiourea to only the sulfinic acid with no detectable sulfenic or sulfonic
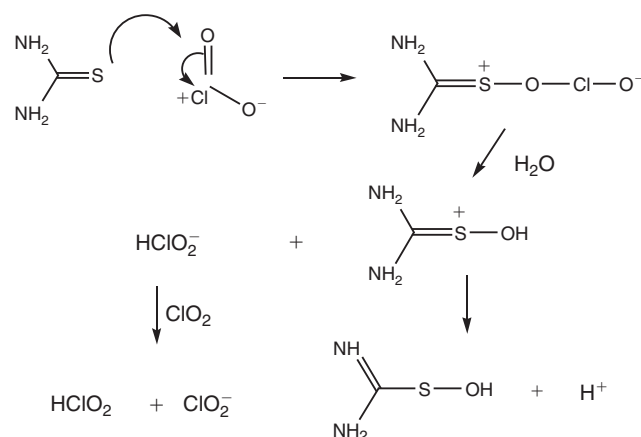
Scheme 2.

acids. This is the method utilised in our laboratories to prepare oxidatively unsaturated thiourea-based sulfur oxo-acids.[31–33]

The strong thiourea peak seen in Fig. 4 favours the route in Reaction 10 over the other possible route that involves an initial homolytic cleavage of the S–S bond to form thiyl radicals:

$$(NH_2C(=NH)S)_2 \rightarrow 2(NH_2)_2CS\cdot \tag{13}$$
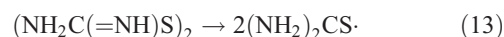
Due to the known stability of FDS, the equilibrium of Reaction 10 lies to the left, and thus the oxidation of FDS is driven by the depletion of the sulfenic acid in the presence of an oxidant. In the absence of an oxidant, the equilibrium in Reaction 10 is maintained indefinitely. Formation of thiourea from Reaction 13 as a precursor would require the hydrogen atom radical which is energetically inaccessible in this reaction medium. No sulfhydryl radicals were observed in this reaction medium on the X-Band EPR spectrometer. Reaction 13 would be much more feasible in aprotic solvents such as acetonitrile.[34]

Chlorine Dioxide Oxidations

In the absence of a free radical mechanism, all oxidation/reductions of the sulfur centre involve a two-electron step. Chlorine dioxide, on the other hand, is expected to proceed, initially, by a two-electron reduction to yield the Cl^{III} species. This is achieved by an initial reduction of Cl^{IV} to an unstable Cl^{II} species, $HClO_2^-$. This chlorite species can then proceed to oxidise the sulfur centers through the now well known mechanism that involves HOCl.[19] We postulate that chlorine dioxide can oxidise thiourea through the formation, initially, of an adduct which can then hydrolyse to yield the sulfenic acid and the aforementioned reduced chlorine^{II} species, $HClO_2^-$. The mechanism is shown in Scheme 2. This reduced, transient and unstable Cl^{II} then reacts with chlorine dioxide to produce the stable Cl^{III} oxidising species. The break-up of the adduct in Scheme 2, coupled with the electron transfer, is assisted by the solvent (water, in this case). This was proved by Olagunju et al. from the observation that chlorine dioxide oxidations were much slower in water–acetonitrile mixtures when compared with water alone as the solvent[35] (pure acetonitrile as solvent was not feasible since the inorganic reagents (sodium perchlorate and sodium chlorite) are insoluble in acetonitrile). Further oxidations of thiourea and thiourea sulfenic acid can be conducted by chlorous acid. This mechanism has been extensively studied and is well known.[21,36]
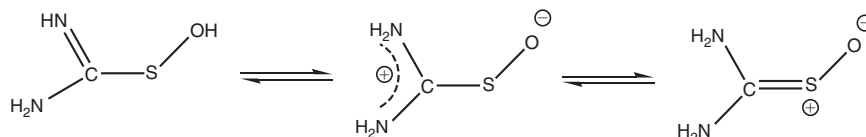
Scheme 3.
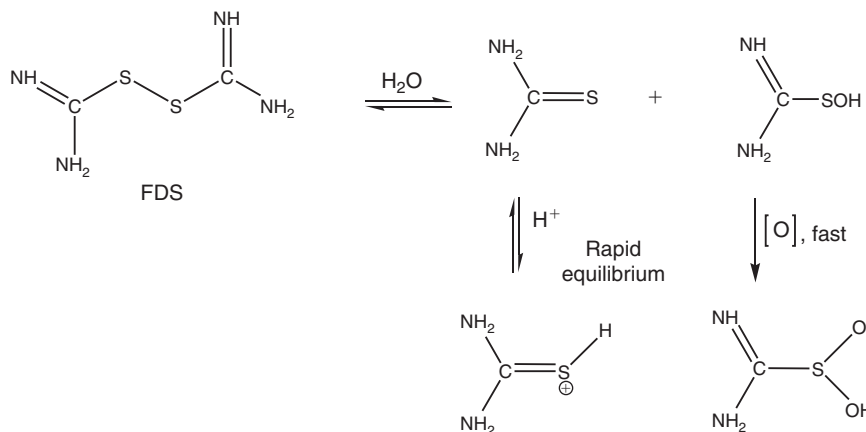
**Scheme 4.** FDS: formamidine disulfide.

The sulfenic acid formed from the hydrolysis of FDS in Reaction 10 is extremely unstable since it does not possess bulky groups that can stabilise the sulfenic acid.[22,23,37] It can exist in three molecular forms; one in neutral form and the other in zwitterionic forms (see Scheme 3). All three forms are highly reactive.

The same $HClO_2^-$ leaving group can be utilised in the further oxidation of the sulfenic acid to the more stable sulfinic acid:

$$NH_2C(=NH)SOH + ClO_2(aq) + H_2O \rightarrow$$
$$(NH_2)(=NH)CSO_2H + HClO_2^- + H^+ \quad (14)$$
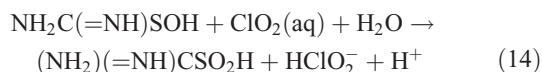
The lack of observation of the sulfonic acid from mass spectrometric data (see Figs 1–4) indicates that the sulfinic acid is oxidised directly to urea and a highly reducing sulfur species. This has been proved consistently in sulfinic acid solutions such as rongalite.[38–40] This ease of cleavage of the C–S bond has been attributed to the elongated C–S bond in thiourea and substituted thiourea dioxides. Deducing purely from the sum of covalent radii, the C–S bond is expected to be 0.179 nm long.[33] Many thiourea oxo-acids have been synthesised in our laboratories and structurally characterised by using X-ray crystallography.[31,33] The C–S bond in thiourea dioxide (aminoiminomethanesulfinic acid, AIMSA), is the second longest at 0.1867 nm. In methyl thiourea dioxide (methylaminoiminomethanesulfinic acid, MAIMSA), it is 0.1860 nm, and in dimethylthiourea dioxide (dimethylminoiminomethanesulfinic acid, DMAIMSA), it is longest at 0.1880 nm.[31] DMAIMSA is the most unstable of this series of oxo-acids, which can be explained by its inordinately long C–S bond.

Thus, further oxidation of the thiourea dioxide should be facile and yield the sulfoxyl anion from sulfoxylic acid, $S(OH)_2$:[41]

$$NH_2C(=NH)SO_2H + H_2O \rightarrow (H_2N)_2C=O + HSO_2^- + H^+ \quad (15)$$
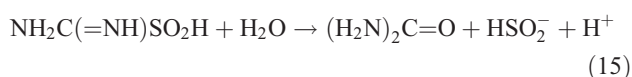
The full oxidation stoichiometry reaction was established, in a previous study, as Reaction 16:[35]

$$NH_2C(=NH)SO_2H + ClO_2(aq) + 2H_2O \rightarrow$$
$$(H_2N)_2C=O + HClO_2^- + HSO_3^- + 2H^+ \quad (16)$$
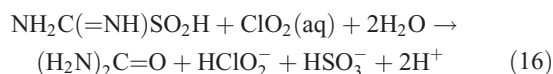
Evidence for Reaction 15 is the observation of an untrapped sulfoxyl anion radical, $SO_2^{\bullet-}$, formed in basic aerobic solutions of sulfinic acids.[40] The sulfoxyl anion radical is formed from its diffusion-controlled reaction with molecular oxygen.

$$HSO_2^- + O_2 \rightarrow SO_2^{\bullet-} + O_2^{\bullet-} + H^+ \quad (17)$$

Due to this very facile reaction, basic thiourea dioxide solutions are used, industrially, as oxygen sponges. Also observed in aerobic basic thiourea dioxide solutions is dithionite, whose precursor is the sulfoxyl anion radical:

$$2SO_2^{\bullet-} \rightarrow S_2O_4^{2-} \quad (18)$$

Effect of Acid

Acid has always been inhibitory in the oxidation of nucleophilic thiols and thiocarbamides. This is due to protonation of the thiol/thiocarbonyl group which reduces the sulfur centre's nucleophilicity, thus making it less susceptible to electrophilic attack. Although oxidations by most oxychlorine species such as chlorous and hypochlorous acid are catalysed by acid, chlorine dioxide has not been known to be affected by acid, except for the variation of its activity in highly acidic conditions. Mass spectrometric data analysis indicates strong peaks for thiourea and thiourea dioxide (indicating Reaction 10 followed by a rapid Reaction 14 (or Reaction 12 in excess reductant) and hence no transient observation of the sulfenic acid). Thiourea formed in Reaction 10 is more nucleophilic and basic than FDS, and would be more easily protonated.

From Scheme 4, this would push the equilibrium of Reaction 10 to the right, resulting in accumulation of thiourea (protonated and unprotonated) and the sulfenic acid. This can effectively catalyse the reaction since FDS is the most inert species in the reaction environment. No simple rate law could be evaluated for an acid effect because subsequent oxidation reactions would involve thiourea, protonated thiourea, and the sulfenic acid.

Conclusion

This mechanistic and kinetic analysis of a component reaction in oxychlorine–thiourea mixtures (Scheme 1) has shown that the FDS–chlorine dioxide reaction is a very important and relevant reaction in the oxidation of thiourea. Mass spectrometric data (Fig. 4) show that in general thiourea oxidations by chlorite, FDS is a major intermediate. Further oxidation of FDS by chlorine dioxide is slower than oxidations of the sulfenic acid (transient not observed in the mass spectrum) and sulfinic acid. It would suggest, then, that further oxidation of FDS to sulfate will be undertaken by other reactive oxychlorine species such as ClO_2^- and HOCl. The comparatively sluggish oxidation of FDS by chlorine dioxide, when compared with the known rapid formation of chlorine dioxide from oxychlorine kinetics ($HOCl + ClO_2^-$; Reaction 5), can explain the oligooscillatory dynamics with respect to chlorine dioxide formation in thiourea–chlorite reactions in acidic medium.

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