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Reactions of methyl viologen and nitrite with thiourea dioxide. New opportunities for an old reductant

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Received 19th September 2002, Accepted 15th October 2002
First published as an Advance Article on the web 25th October 2002

Thiourea dioxide was used as a precursor for sulfoxylate, SO_2^{2-}, which is shown to reduce the methyl viologen dication to the fully reduced form, this is the first example of a direct study of the reduction with sulfoxylate; an important advantage of sulfoxylate and its parent compound thiourea dioxide, is their ability to reduce nitrite (the final product being nitrogen) and nitrous oxide in alkaline solutions in the absence of a catalyst.

The sulfur dioxide anion-radical SO_2^- is a well-known inorganic radical that has a strong reducing ability.[1] Published data indicate that the Marcus theory is applicable to the SO_2/SO_2^- couple.[2] In most studies devoted to electron exchange in this couple, dithionite serves as a source of SO_2^-. It is noteworthy that the SO_2^-/SO_2^{2-} couple in which SO_2^- is the oxidized form has not been studied to date. Recently,[3] data on the aerobic decomposition of thiourea dioxide, $(NH_2)_2CSO_2$ (TDO), indicated that this compound can be used as a precursor for the reduced form in this couple, *viz.* sulfoxylate SO_2^{2-}, and this species may be easily oxidized to SO_2^-. The unusual sulfur species sulfoxylate is quite interesting from both theoretical and practical points of view. The need to study its properties is not only due to its high reducing ability, but also due to the fact that sulfoxylate is the possible intermediate in the oxidation of hydrogen sulfide.[4] Here we report studies on the reactions of thiourea dioxide with methyl viologen and nitrite that demonstrate distinctive differences in the reactivity of sulfoxylate and the sulfur dioxide anion radical.

SO_2^- readily reduces methyl viologen, MV^{2+}, to give the strongly coloured blue cation-radical, MV^+ (λ_{max} = 600 nm, ε = 14000 M^{-1} cm^{-1}).[5] In the course of our studies on thiourea dioxide it was found that in alkaline solutions (0.05 to 0.5 M KOH) under rigorously anaerobic conditions, thiourea dioxide reduces MV^+ further to the formation of an orange species. This reduction is accompanied by formation of dithionite (λ_{max} = 315 nm, ε = 8043 M^{-1} cm^{-1}).[6] Comparison of the optical spectrum (λ_{max} = 388 nm, ε = 26000 M^{-1} cm^{-1}) with literature data,[7] showed that the fully reduced form of methyl viologen, MV^0, was obtained. Unfortunately, our attempts to obtain NMR spectra of the suggested fully reduced form of methylviologen in aqueous solutions were unsuccessful in the absence of a stabilizer. During the preparation of the samples, formation of the blue MV^+ species was observed, presumably due to the reaction of MV^0 with water (MV^0 is known to react spontaneously with water, irrespective of pH).[8] We, however, found that addition of CS_2 significantly stabilized aqueous solutions of MV^0. This observation created the possibility to prepare stable, air-free solutions of the MV^0–CS_2 adduct and to record its ^1H- and ^{13}C-NMR spectra.† Interestingly, introduction of oxygen to alkaline solutions of MV^0 in the presence of an excess of both dithionite and TDO, leads to the formation of the cation-radical MV^+, but further production of sulfoxylate during the decomposition of TDO converts MV^+ back to MV^0 at its initial concentration again. This clearly indicates that MV^0 is stable in alkaline solutions of TDO.

The kinetics of the $MV^+ \longrightarrow MV^0$ reaction step was studied under an argon atmosphere in 0.1 M KOH by using the stopped-flow technique under pseudo-first-order conditions. The rate of the reaction strongly depended on the age of the TDO alkaline solutions: the older the solution, the higher the rate. This only applied to the first three to four hours after TDO had been dissolved in aqueous alkaline solution. At longer times, *i.e.* after complete decomposition of TDO and formation of SO_2^{2-} and urea (which is known to be the main nitrogen-containing decomposition product of thiourea dioxide in strongly alkaline solutions),[1b] the rate of the reaction $MV^+ \longrightarrow MV^0$ did not depend on the age of the TDO solution during the subsequent 24 h. These results show that SO_2^{2-} is stable in alkaline solution under anaerobic conditions and that it can keep its reducing ability over a long time. This observation created the possibility to study the reaction between sulfoxylate and the cation-radical MV^+ directly as shown in reaction (1), using aged solutions of TDO (term “aged solutions” means solutions stored for 4–24 h). The value of the rate constant for this reaction at 25 °C was found to be 1400 ± 140 M^{-1} s^{-1} (0.1 M KOH, 298 K).

$$SO_2^{2-} + MV^+ \longrightarrow SO_2^- + MV^0 \qquad (1)$$

The sulfur dioxide anion-radical produced in reaction (1), dimerizes further to give dithionite in reaction (2).

$$2SO_2^- \rightleftharpoons S_2O_4^{2-} \qquad (2)$$

Reactions (1)–(4) can account for the redox cycling shown in Fig. 1 if $[SO_2^{2-}] > [O_2]$.

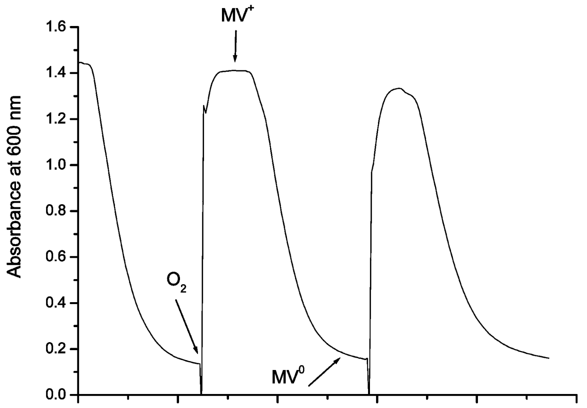


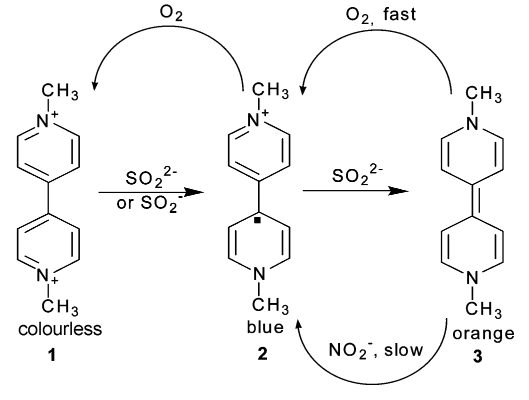
Fig. 1 Redox cycling observed in the system MV^0–SO_2^{2-}–O_2 in 0.1 M KOH, 25 °C, $[MV^0]$ = 1.43 × 10^{-2} mM, [TDO] = 2.7 mM.

DOI: 10.1039/b209195j

$$MV^0 + O_2 \rightleftharpoons MV^+ + O_2^- \qquad (3)$$

$$SO_2^{2-} + O_2 \rightleftharpoons SO_2^- + O_2^- \qquad (4)$$

The presence of an excess of reductants (sulfoxylate and dithionite) prevents the oxidation of MV^+ to MV^{2+}. Since MV^+ is formed on the introduction of oxygen into the system in the presence of sulfoxylate (see Fig. 1) it can be concluded that reaction (3) proceeds much faster than (1). It should be noted, however, that a complete description of the reactions in the thiourea dioxide–methylviologen–oxygen system should also include subsequent reactions of for instance superoxide. The possible redox transformations of MV^{2+} in the presence of sulfoxylate and different oxidants are shown in Scheme 1.



Scheme 1

To the best of our knowledge, the reaction described above is the first example of the chemical reduction of MV^+ to MV^0 in aqueous solution. There is a report in the literature that describes the formation of MV^0 *via* slow reduction of MV^+ with dithionite.[9] However, we were unable to reproduce this experiment. During the reaction of an excess of dithionite with MV^+, the formation of an orange–brown species was observed, but this product could not be oxidized quantitatively to the initial MV^{2+}. In all other literature, reference is made to the synthesis of MV^0 *via* 'aqueous electrochemical'[10] or 'non-aqueous' (by Mg in MeCN or Na in THF)[7] reduction of MV^+. Due to the importance of viologens in photochemistry,[11] biochemistry[12] and Marcus-type calculations,[2] our findings may be of more general interest. It should be noted that the authors of ref. 9 reported a value of E^0 for the MV^+/MV^0 redox couple of -1.04 V (relative to SCE). Despite the fact that in light of our observations this value should be used with care, it may serve for the preliminary estimation of E^0 for the SO_2^-/SO_2^{2-} couple.

The application of viologens as one-electron transfer agents may also be useful in studies on the reactions of thiourea dioxide with compounds that are difficult to reduce. In this study, methyl viologen was employed for a simple spectrophotometric monitoring of the reaction between TDO and nitrite ion in alkaline aqueous solutions.

Preliminary studies showed that dithionite does not react with nitrite in the absence of a catalyst. Therefore, it was possible to use nitrite for the conversion of MV^0 to MV^+ (see Scheme 1). This approach allowed us to exclude the first fast reaction $MV^{2+} \longrightarrow MV^+$, and simplify the overall scheme to only the second reversible step. Typical kinetic traces recorded at 600 nm are shown in Fig. 2. The presence of an induction period in the kinetic traces, which correlates with the concentration of TDO employed, unequivocally indicates that the reaction between sulfoxylate and nitrite does occur, since the oxidation of MV^0 to MV^+ (the rapid increase in absorbance following the induction period) can only proceed when SO_2^{2-} is used up. The possibility of nitrite reduction by SO_2^{2-} in alkaline solutions (0.1 to 0.5 M NaOH) could be proven in a direct reaction of TDO with sodium nitrite. It was shown that under anaerobic conditions, this reaction is accompanied by the formation of dithionite, *i.e.*, a one-electron oxidation of SO_2^{2-} to SO_2^-, followed by the dimerization of the sulfur dioxide anion radical to dithionite (reaction 2). Thus the primary step in the reaction under investigation may be formulated as follows:

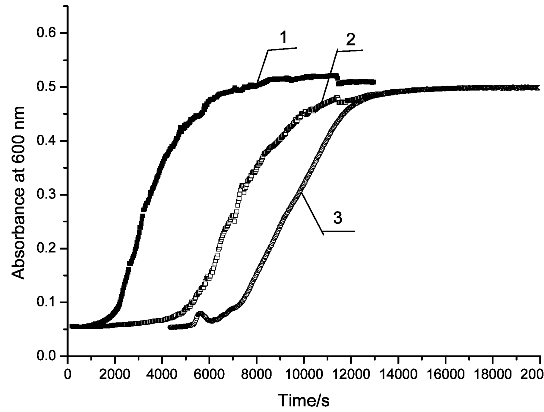


Fig. 2 Formation of the cation radical **2** in the reaction of nitrite and **3** in the presence of TDO in 0.1 M KOH, 25 °C; [**3**] = 3.6×10^{-2} mM; [$NaNO_2$] = 60 mM; [TDO] = 1.9 mM (1); 3.8 mM (2); 4.5 mM (3).

$$SO_2^{2-} + NO_2^- \longrightarrow SO_2^- + NO_2^{2-} \qquad (5)$$

The hydronitrite radical NO_2^{2-} is known to be a product of the reaction of e_{aq}^- and nitrite.[13] This unstable species rapidly decays to NO in aqueous solution:

$$NO_2^{2-} + H_2O \longrightarrow NO + 2OH^- \qquad (6)$$

It should be noted, however, that the presence of NO in the products of the reaction between TDO and nitrite was not observed. Instead of NO, ^{15}N NMR and MS analyses indicated the presence of $^{15}N_2O$ (-181.5 and -216.7 ppm) and $^{15}N_2$ (*m*/*z* 30). These results show that not only NO, but also N_2O reacts with sulfoxylate (nitric oxide can react with dithionite as well;[14] however, our experiments showed that the reaction of N_2O and $S_2O_4^{2-}$ does not proceed significantly). The possible reduction of nitrous oxide by sulfoxylate was proven by direct experiments. Similarly to the reaction with nitrite, reduction of N_2O is accompanied by the accumulation of dithionite (Fig. 3) which provides evidence for a one-electron reduction process.

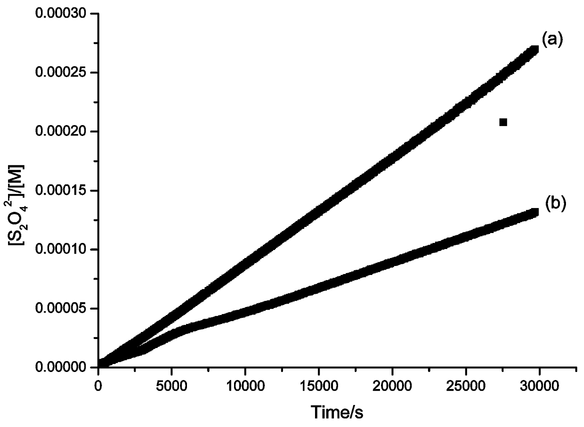


Fig. 3 Time-dependence of [$S_2O_4^{2-}$] during the reaction of N_2O with TDO in 0.1 M KOH solution. [TDO] = 1.07×10^{-2} M, [N_2O] = ½ saturated (a), ¼ saturated (b).

The possibility to reduce nitrite in strongly alkaline solutions in the absence of a catalyst, is an important advantage of TDO. Most of the known reductions of nitrite were investigated in acidic and neutral media.[15] In basic solutions the reaction of nitrite, for instance with sodium borohydride, does not take place unless $Cu(OH)_2$ is present.[16] Reduction by hydrazine is also a catalytic process.[17]

Nitrous oxide is also a compound that is difficult to reduce (Fig. 3). Although N_2O is reducible by hydrated electrons and super-reduced states of some transition metals, it is stable toward many common reducing agents.[18] Therefore, a new example of its non-catalytic reduction reported in this paper may be of more general interest.

In conclusion, interesting examples of new applications of the powerful reducing agent thiourea dioxide were found. The results of this study open new perspectives for the application of thiourea dioxide as a unique reductant and source for sulfoxylate. A study of the detailed reaction mechanisms of reactions reported here is presently in progress.

Acknowledgements

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and DAAD (fellowships to E. V. K. and S. V. M.).

Notes and references

† All chemicals of analytical reagent grade were purchased from Sigma-Aldrich and used without further purification. Since the reactivity of TDO in alkaline solutions depends on its age in all experiments (if not specified) fresh solutions were used. 95% ^{15}N labeled $NaNO_2$ was used for the ^{15}N-NMR experiments (solutions in D_2O and ^{15}N nitromethane as reference) and gas-phase MS monitoring.

Conventional kinetic experiments were performed on Cary 1 or Cary 5 UV-Vis spectrophotometers under anaerobic conditions. A thermostatted (± 0.1 °C) Applied Photophysics SX 18 MV stopped-flow spectrophotometer with an observation path length of 1.0 cm was used to follow the faster reactions. NMR measurements were performed using a Bruker Avance DRX400 WB spectrometer equipped with a superconducting BS-94/89 magnet system at 40.56 MHz for ^{15}N and 400.13 MHz for ^1H. Mass spectra were recorded on a JEOL Mstation spectrometer.

Analytical data for adduct $MV°–CS_2$. ^1H NMR (300 MHz, D_2O : $[D_6]$DMS (1 : 1), CS_2, 25 °C, TMS): δ 4.9 (s, 4H, CH), 4.5 (s, 4H, CH), 4.1 (t, ^3J(H,H) 1.9 Hz, 6H, CH_3). ^{13}C NMR (75.47 MHz, D_2O : $[D_6]$DMS (1 : 1), CS_2, 25 °C, TMS) δ 20.3, 20.6, 20.9, 21.1, 123.2, 128.6. UV/Vis (H_2O): λ_{max} (ε) 388 nm (26000 M^{-1} cm^{-1}).

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