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## COMMUNICATION

## The ring opening reaction of 1, 3-dithiol-2-one systems is fully reversible

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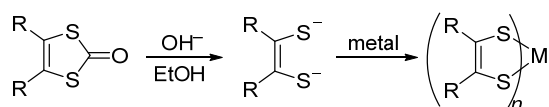
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**The deprotection of a common precursor moiety in dithiolene chemistry was discovered to be fully reversible, which, besides being relevant for researchers working in very different fields with these non-innocent ligand systems, may even have an impact on CO<sub>2</sub> housekeeping as the deprotected ligand acts as a respective trap.**

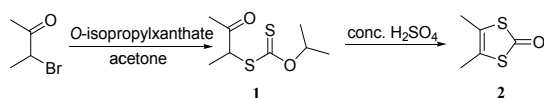
The 1, 3-dithiol-2-ones comprise a class of molecules with demonstrated synthetic utility for the synthesis of metal dithiolene complexes, tetrathiafulvalenes and related materials. Due to the ligands' *non-innocent* character and the rich electrochemical and photophysical behavior associated with metal dithiolene complexes, a variety of research fields exploits these systems regularly. Investigations are for instance aimed at applications such as molecular conductor materials<sup>1</sup>, ferromagnets<sup>2</sup>, sensing devices<sup>3</sup>, IR dyes<sup>4</sup>, catalysis<sup>5</sup>, liquid crystals<sup>6</sup> and others. In order to generate dithiolene metal complexes from 1, 3-dithiol-2-ones the C=O moiety needs to be released from the precursor in basic conditions, which is most commonly done using ethanolic alkaline metal hydroxide solution (Scheme 1)<sup>7</sup>. The typical excess of hydroxide described in the literature lies in between 2 and 5<sup>3a, 8</sup> per ligand precursor; in some cases even higher<sup>9</sup>. However, the minimum or exact stoichiometry needed for a successful yet complete de-protection of the dithiolene has not been investigated comprehensively so far.



Scheme 1. Release of C=O moiety from 1, 3-dithiol-2-ones ring in basic conditions in order to generate metal-dithiolene complexes.

Further, it is not clear, how these values were derived and if it may not be better to work at the lowest possible base concentrations in specific cases. In ongoing work towards investigating dithiolene compounds by UV-Vis methods it had become important for us to work at the lowest possible excess of base due to potentially base sensitive substituents and reaction partners. Therefore quite a number of titration experiments have been conducted in order to determine the optimal amount of base. The optimum base:precursor ratio was found to be 2.5:1. This was, however, not the most interesting finding in course of conducting these experiments. To our great surprise and entirely by chance it was found, that the de-protection reaction in basic solution was actually fully reversible by addition of an equal amount of acid. This finding sheds some light on the side products of the de-protection reaction and allows more insight into its mechanism, which is of interest for all who are working in the large variety of research fields depending on this reaction. Possibly even more importantly: this behavior together with the proposed mechanism (explained below) suggests, that dithiolate salts may be useful traps for CO<sub>2</sub>.

For the initial titration experiments one of the simplest, symmetrically substituted compounds bearing the 1, 3-dithiol-2-one moiety was chosen: 4, 5-dimethyl-1, 3-dithiol-2-one. Besides being rather simple and therefore easy to handle and characterize, from a synthetic point of view this compound should be easily modifiable for instance by bromination of the methyl group and subsequent nucleophilic substitution<sup>10</sup>. This makes it an interesting starting material for differently substituted dithiolenes. It has also been used

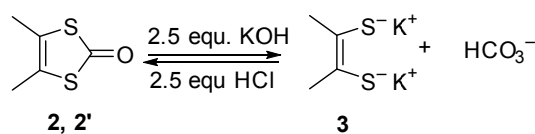


Scheme 2. Synthetic route and molecular structures of compound **1** and **2**.

as is as ligand system for molybdenum and tungsten oxidoreductase enzyme model complexes<sup>11</sup>.

4, 5-dimethyl-1, 3-dithiol-2-ones can be synthesized by several distinct synthetic routes.<sup>12</sup> The procedure to 4, 5-dimethyl-1,3-dithiol-2-ones beginning with the reaction between 3-bromo-2-butanone and an *O*-alkylxanthate salt to afford an *O*-alkyl *S*-3-oxobutan-2-yl dithiocarbonate intermediate, which is then subjected to acid catalyzed ring closure<sup>10a, 13</sup> was applied in this work and is shown in Scheme 2. The crude product constitutes a black oil, which was purified using a short-path fractional distillation followed by crystallization from hexane to obtain off white colored crystals. The crystal structural parameters of compound **2** are the same as those having been reported before<sup>14</sup> and both compounds (**1** and **2**) were characterized by elemental analysis, mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies (see ESI† for details).

The base hydrolysis of 1, 3-dithiol-2-one ring systems was standardized in course of ongoing work to use 2.5 equivalents of strong base like potassium hydroxide or cesium hydroxide per ligand precursor. Compound **2** was treated with 2.5 equivalents of KOH under nitrogen atmosphere and after 2h the completion of base hydrolysis was confirmed by <sup>13</sup>C NMR. The disappearance of the signal at  $\delta$  191.9 ppm from compound **2** demonstrates the de-protection of the dithiolene ligand by hydrolysis of the keto group. The appearance of new signals at  $\delta$  161 and 158 ppm in compound **3** has been assigned to the formation of carbonates as side products and sheds light on the mechanism of deprotection by KOH (see Figure S3 and S5). When 2.5 equivalents of conc. hydrochloric acid were added to the de-protected form of the dithiolene ligand (**3**), it surprisingly returned to its previous protected form (now denominated compound **2'**), revealing a full ring opening-closing reversibility of 4, 5-dimethyl-1, 3-dithiol-2-one under basic and acidic conditions (Scheme 3).



Scheme 3. Ring opening-closing reversibility of 4, 5-dimethyl-1, 3-dithiol-2-ones under basic and acidic conditions.

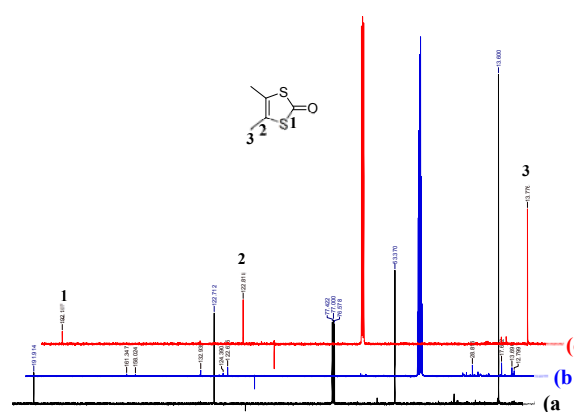
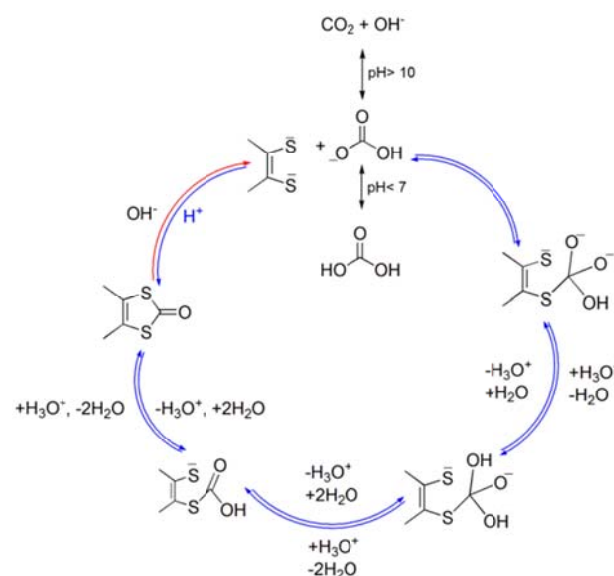


Figure 1. <sup>13</sup>C NMR spectrum of (a) 4, 5-dimethyl-1, 3-dithiol-2-ones **2**, (b) 2, 3-dimethyl-1,4 dithiolate **3** and (c) reformed 4, 5-dimethyl-1, 3-dithiol-2-ones **2'**.

Reappearance of the NMR signal at  $\delta$  192 ppm in <sup>13</sup>C NMR (Figure 1) confirms the reformation of the 1, 3-dithiol-2-one ring upon addition of 2.5 equivalents of conc. HCl to species **3** (the de-protected salt).

The proposed mechanism for the reformation of the 1, 3-dithiol-2-one ring in presence of enough acid to neutralize the solution is illustrated in Scheme 4. The first step involves bond formation between one of the dithiolate sulfur atoms and the hydrogen carbonate carbon aided by acid, which will be protonated again to give an intermediate bearing two hydroxyl groups. In the next step, one of the hydroxyl groups is released to form the C=O bond. This promotes the second thiolate to attack it, reforming the ring by



Scheme 4. Proposed mechanism for the reformation 1, 3-dithiol-2-ones ring.

release of a water molecule to give the stable closed structure, i.e. the 1, 3-dithiol-2-one ring. Although DFT calculations on aqueous acid base systems are particularly difficult to execute and the results certainly have to be taken very cautiously, such calculations have been done and they support the proposed mechanism. The respective calculated energy levels are shown in Figure S12 along computational details in the ESI.

Apparently, under neutral pH-conditions the reformation of the ring from the dithiolate is favorable compared to a dissociation of carbonic acid into water and CO<sub>2</sub>. Consequently, ene-dithiolate salts may be quite efficient traps for CO<sub>2</sub> in aqueous solutions.

The observed ring opening-closing reversibility was also confirmed by monitoring the C=O stretching frequency in the infrared spectra of compounds **2**, **3** and **2'** (Figure 2). 4, 5-dimethyl-1, 3-dithiol-2-one (**2**) displays a band at 1753 cm<sup>-1</sup> caused by its C=O group, which disappears in compound **3** after de-protection of the dithiolene ligand. The band, based on the keto group, can be regenerated by addition of conc. HCl to compound **3**. This confirms that in the presence of enough acid to neutralize the solution compound **3** regenerates its precursor, i.e. the full ring opening-closing reversibility of the 4, 5-dimethyl-1, 3-dithiol-2-one system.

The UV-Vis spectra of compounds **2**, **3** and **2'** are displayed in Figure S11 and reveal a change of absorbance intensity with ring opening and closing of the 1, 3-dithiol-2-one ring system (Figure 3). The absorbance at 273 nm is most likely due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  mixed transitions. In the open form of the dithiolene ligand the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions are expected to be stronger causing an

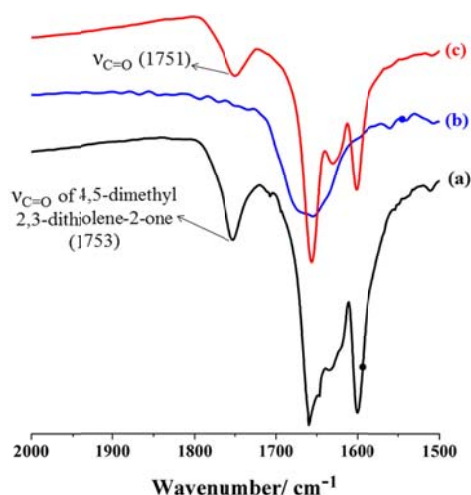


Figure 2. IR spectra of (a) 4, 5-dimethyl-1, 3-dithiol-2-ones **2**, (b) 2, 3-dimethyl-1,4 dithiolate **3** and (c) reform 4, 5-dimethyl-1, 3-dithiol-2-ones **2'** in KBr Pellets.

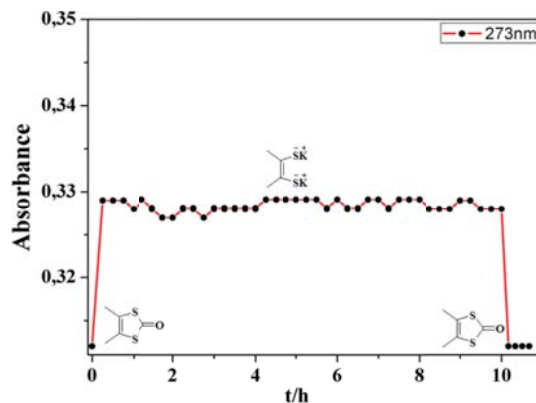


Figure 3. The above spectra shows the generation and the stability of the intermediate 2, 3-dimethyl-1, 4 dithiolate (**3**) with time and reformation of the 1,3-dithiol-2-one upon addition of acid (at  $\lambda_{\max} = 273\text{nm}$ ) at hour 10.

increase of absorbance intensity ( $\epsilon$ , 6592 cm<sup>-1</sup>mol<sup>-1</sup>L) compared to the closed form ( $\epsilon$ , 6240 cm<sup>-1</sup>mol<sup>-1</sup>L). Upon addition of acid to the open form the  $\epsilon$  values come back exactly to 6240 cm<sup>-1</sup>mol<sup>-1</sup>L, corroborating the reformation of 4, 5-dimethyl-1, 3-dithiol-2-one ring.

In conclusion, we have demonstrated how easily the ring opening and ring closing reactions of the 1, 3-dithiol-2-one system can be controlled simply by adjusting the pH-value of the solution. The full reversibility of the ring opening reaction was confirmed by <sup>13</sup>C NMR, IR and UV-vis spectroscopy. The proposed respective reaction mechanism is supported by DFT calculations. These results also show ene-dithiolate salts to be potentially quite efficient traps for CO<sub>2</sub> in aqueous solution; a property that warrants further investigation. At the very least, these findings will help many researchers in a variety of different fields to optimize their reaction conditions when working with 1, 3-dithiol-2-ones and to understand in more detail what is going on in their reaction mixtures.

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## Notes and references

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†Electronic Supplementary Information (ESI) available: Syntheses, experimental and computational details, IR, NMR and UV-vis spectra. See DOI: 10.1039/c000000x/

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