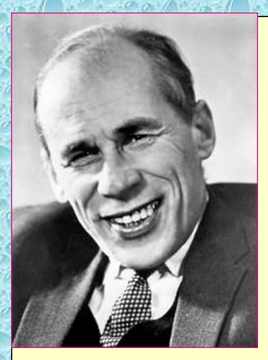

Photochemistry of Sodium Thiosulfate in Aqueous Solutions: a Lot of Radicals

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Why Thiosulfate?

1

- Sodium thiosulfate (*hypo*) is widely used in industry and medicine
  - Historically it was employed in photography to fix black and white negatives and prints after the developing stage
  - Leaching agent in gold metallurgy
  - Wastewater purification etc.
  - Detoxifying and antihistamine active agent
- $S_2O_3^{2-}$ in photochemistry
  - Photochemical splitting of H_2S into hydrogen and sulfur
  - Additive for photovoltaic solar cells
  - Photochemical synthesis of thioperrhenates (N.B. Egorov)

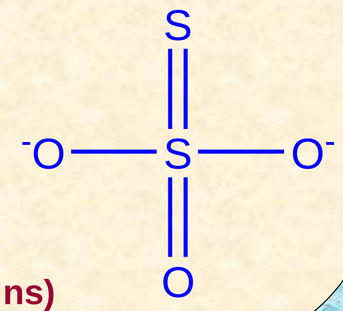
However mechanism of photochemical reactions remains unclear.

Goal

- Mechanistic study of $S_2O_3^{2-}$ photochemistry

Methods

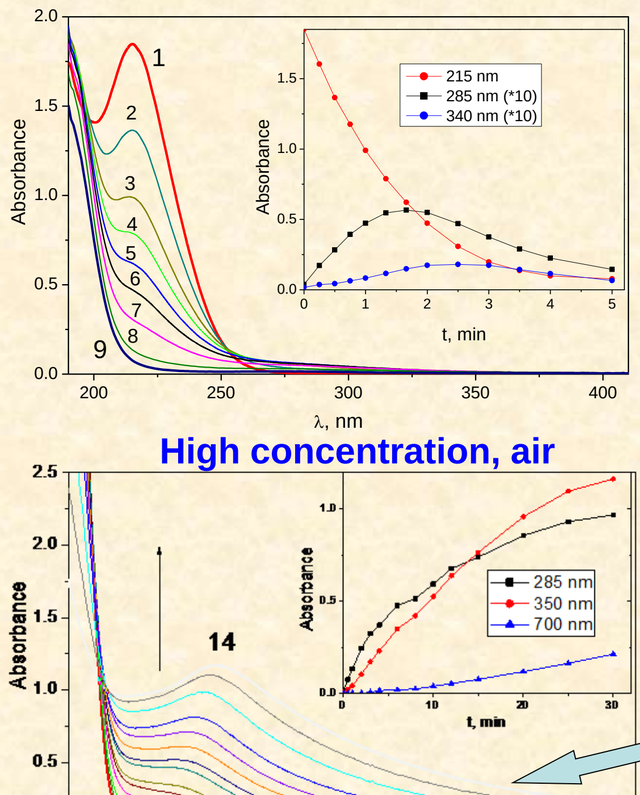
- Steady-state photolysis
- Laser flash photolysis (YAG laser, 266 nm, 5 – 6 ns)



Stationary Photolysis

2

Low concentration, air



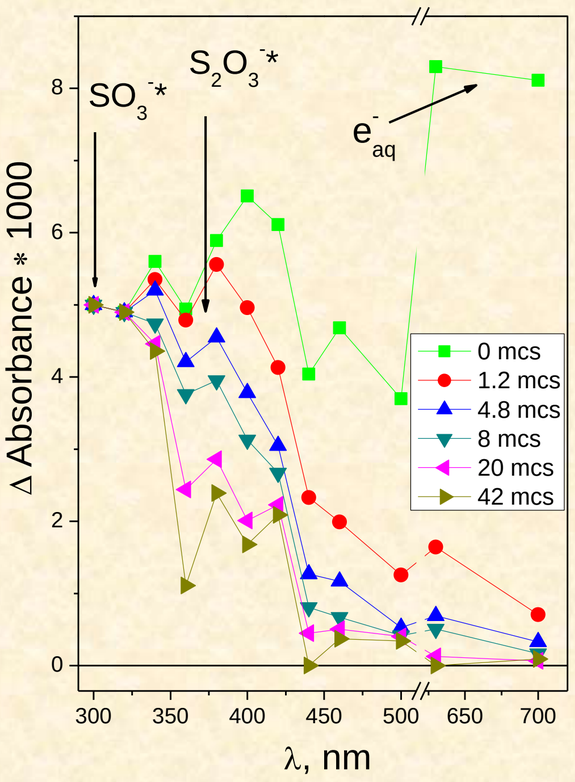
- Excitation at 222 nm
  - CCTS type band
- Oxygen-dependent process
- Stable products:
  - Tetrathionate $S_4O_6^{2-}$
    - secondary photolysis
  - SO_3^{2-}
  - SO_4^{2-}
  - S_8 and S_n (n = 6, 7, 9, 12)
  - Sols – in the presence of O_2

High concentration, air

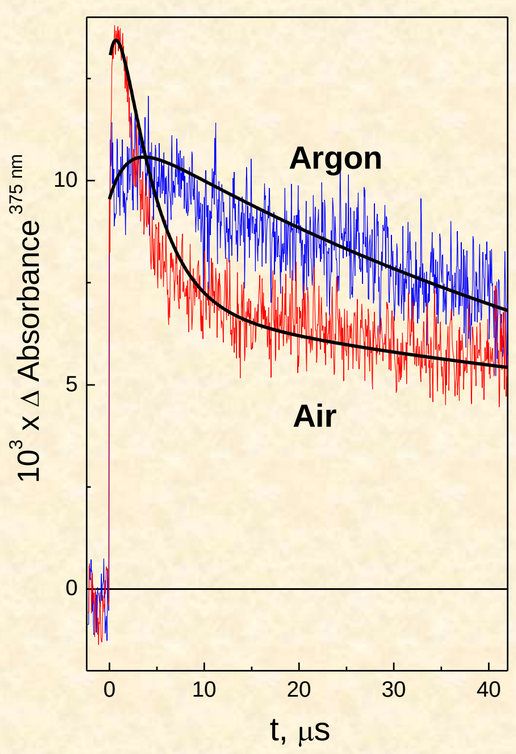
Raffo sol formation. Contains of polymeric sulfur S_n and polythionic acids $H_2S_mO_6$

Laser Flash Photolysis (266 nm)

3



Intermediate absorption in Ar-saturated solution.



Kinetic curves at 375 nm fitted using complete reaction scheme.

Three Channels of Photolysis

4

Channel 1 (O_2-independent, selected reactions)

$$S_2O_3^{2-} \xrightarrow[H_2O]{h\nu} S_2O_3^{\bullet-} + e_{aq}^-$$

$$S_2O_3^{2-} \xrightarrow[H_2O]{h\nu} S^{\bullet-} + SO_3^{\bullet-}$$

$$S_2O_3^{\bullet-} + S_2O_3^{\bullet-} \rightarrow S_4O_6^{2-} \qquad 3.8\times10^8\ M^{-1}s^{-1}$$

$$e_{aq}^- + S_2O_3^{2-} \rightarrow S^{\bullet-} + SO_3^{2-} \qquad 1.6\times10^8\ M^{-1}s^{-1}$$

$$S_2O_3^{\bullet-} + S_2O_3^{2-} \Leftrightarrow {}^{\bullet}S_4O_6^{3-} \qquad \rightarrow 2.4\times10^6\ M^{-1}s^{-1}\ \leftarrow 1.5\times10^5\ s^{-1}$$

$$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow SO_3^{2-} + SO_3 \qquad 1.7\times10^8\ M^{-1}s^{-1}$$

$$S^{\bullet-} + S^{\bullet-} \rightarrow S_2^{2-} \qquad 6.3\times10^8\ M^{-1}s^{-1}$$

$$nS \rightarrow S_n$$

$$nS + 2SO_3^{2-} \rightarrow S_n(SO_3)_2^{2-}$$

$$S + SO_3^{2-} \rightarrow SSO_3^{2-}$$

For ionic reactions I = 0.

Oxygen-Dependent Channels of Photolysis

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Channel 2

$$S^{\bullet-} + O_2 \rightarrow SO_2^{\bullet-}$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$$

$$O_2^{\bullet-} + S_2O_3^{2-} \rightarrow SO_2^{\bullet-} + SO_3^{2-}$$

$$SO_2^{\bullet-} + O_2 \rightarrow SO_2 + O_2^{\bullet-}$$

$$SO_2 + H_2O \Leftrightarrow 2H^+ + SO_3^{2-}$$

- In the presence of dissolved oxygen Channel 1 should be extended
- Chain process!
- $O_2^{\bullet-}$ is a chain carrier
- Acidification accelerates sol formation

Channel 3

$$S_2O_3^{2-} + O_2 \rightarrow [S_2O_3^{2-}...O_2]$$

$$[S_2O_3^{2-}...O_2] \xrightarrow{h\nu} S_2O_3^{\bullet-} + O_2^{\bullet-}$$

$$[S_2O_3^{2-}...O_2] \xrightarrow{h\nu} SO_3^{\bullet-} + SO_2^{\bullet-}$$

- Increase of $S_2O_3^{\bullet-}$ and $SO_3^{\bullet-}$ yields in the presence of O_2
- Photolysis of weakly-bound complex formed by $S_2O_3^{2-}$ and O_2

About weakly-bound van der Waals complexes see e.g. [A.V. Baklanov, D.H. Parker, *Kinet. Catal*. 61 (2020) 174] and other works of A. Baklanov group.

Sulfur-Containing Radicals

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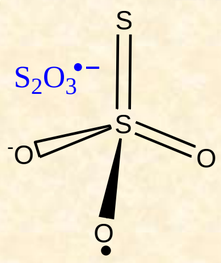
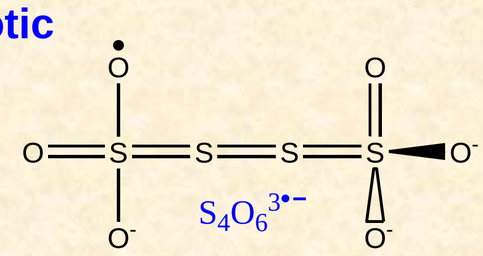
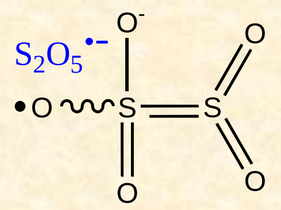
Exotic

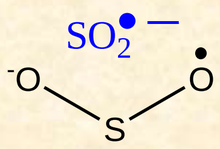


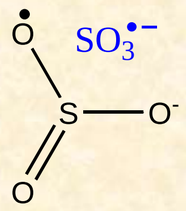


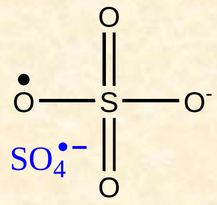
Proposed by us

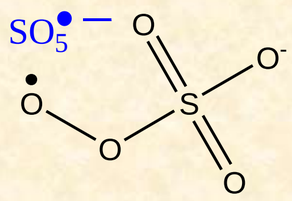


Common









In Conclusion

- Mechanism of thiosulfate photolysis was proposed
- 16 rate constants were measured or estimated
- Quantum chemical calculations of the radicals electronic absorption spectra are in progress