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Publication Date

1983-08-01

LBL-16605
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE
DIVISION

Submitted to High Temperature Science

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August 1983

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-16605

Study of the Disproportionation of Sodium Thiosulfate by X-ray Photoelectron Spectroscopy**

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** This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environment Control Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.

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Abstract

The disproportionation of sodium thiosulfate to form sodium sulfite and elemental sulfur has been studied in the temperature range 495-548°K by means of x-ray photoelectron spectroscopy (XPS). The disproportionation started with an induction period, followed by a steady state disproportionation rate regime, and ended up with a diffusion rate controlling process. The duration of the induction period was inversely proportional to the temperature of heating. The disproportionation in the steady state regime followed a first order reaction rate law with the enthalpy and entropy of activation $H^{\neq}$ = 26.0 Kcal/mol and $S^{\neq}$ = -14.9 e.u.

Introduction

Thiosulfates are thermally unstable and decompose to form sulfite and elemental sulfur with heat treatment. The kinetics of disproportionation of thiosulfates has not been investigated however. This knowledge is needed in power plant flue gas clean-up industry where thiosulfates can be generated or are employed as an additive in some flue gas desulfurization processes.[1] In this paper, we report this kinetic information obtained by means of x-ray photoelectron spectroscopy.

Experimental Methods

Sodium thiosulfate samples were prepared by spraying an aqueous solution of 1% $Na_2S_2O_3$ from a glass nebulizer onto clean aluminum foils (~6x12 mm) and then dehydrated by heat treatment in an oven at 338°K for at least 24 hrs. The average thickness of the sample material on the aluminum foil was calculated from the total sulfur content determined by x-ray fluorescence analysis and the morphology of samples depicted by an ISI Model DS-130 scanning electronmicroscopy (SEM).

The kinetics of disproportionation of sodium thiosulfate was studied by means of an AEI ES200 photoelectron spectrometer utilizing Al K x-ray (1486.6 eV) with a sample chamber pressure of less than 10^{-8} torr during measurements. Samples were heated by a resistance heating element in the sample holder under vacuum. The XPS spectrum of the S ($2p_{1/2,3/2}$) region of $Na_2S_2O_3$ samples was taken periodically after samples had reached a desired temperature. The temperature range studied was 495-548^{o}K. The kinetic data were obtained from the change of XPS spectrum intensity of reduced sulfur (S^{2-}) in $Na_2S_2O_3$ as a function of heating time at a given temperature.

Results and Discussion

SEM results showed that sodium thiosulfate was in clusters of aggregates scattered on the aluminum foil. An average thickness of about 20 nm was calculated for these aggregates from the area projected for the aggregates and the determinations of their sulfur contents by x-ray fluorescence technique. The density of sodium thiosulfate was assumed to be 1.667.[2]

Figure 1 illustrates the use of XPS in monitoring the changes in concentrations of oxidized and reduced sulfur species during the course of the sodium thiosulfate disproportionation. The binding energies of the Sulfur $2p_{1/2,3/2}$ electrons of oxidized (S^{6+}) and reduced (S^{2-}) sulfur in sodium thiosulfate are 168.4 and 162.3 eV respectively. Both types of sulfur species show approximately the same intensity (Fig. 1a). XPS intensity of the reduced sulfur decreased along with the heating as shown in Fig. 1b-f. Whereas the intensity (measured by integrating the peak area) of the oxidized sulfur remains constant, there is a small shift in the binding energy toward the low energy side. We attribute this shift of binding energy to the chemical conversion of $Na_2S_2O_3$ to Na_2SO_3. The binding energy of the sulfur $2p_{1/2,3/2}$ electrons in Na_2SO_3 is 166.7 eV which is too close to that of oxidized sulfur in $Na_2S_2O_3$ to be resolved with the XPS spectrometer employed for this experiment.

The production of elemental sulfur could not be detected by XPS techniques because of the vaporization under high vacuum and temperature conditions employed. The major sulfur vapor species at temperatures employed in this experiment (495-548K) in S_2.[3] The disproportionation of thiosulfate can be represented as

$$Na_2S_2O_3 \rightleftarrows Na_2SO_3 + 1/2S_2\uparrow$$

The rate equation of a first-order reaction can be expressed as

$$\ln C_o/C = k(t-t_o)$$

where C_o and C is the concentration of reactant at time t_o and t respectively, k is the rate constant. Figure 2 is a typical curve of the plot of ln C_o/C vs. t for the disproportionation of sodium thiosulfate. The concentration ratio of reactant C_o/C was taken as the intensity ratio of the undecomposed reduced sulfur at time t_o to t (normalized to the intensity of the oxidized sulfur) as observed by XPS. This Figure suggests that the disproportionation might begin with an induction period (section I), followed by a steady state regime (section II), and end with a period where the diffusion rate of species from the bulk to surface seems to be the controlling factor (section III). The duration of the induction period was shorter and the steady state disproportionation rate was faster with the increase in temperature.

The effect of temperature changes on the steady state disproportionation decomposition rate constants is shown in Figure 3. When the transition-state theory[4] is applied, the rate constant for the disproportionation of $Na_2S_2O_3$ can be expressed as

$$k \geq (k'T/h)\ e^{S^{\neq}/R}\ e^{-H^{\neq}/RT}$$

where k′ and h are Boltzmann and Planck constants respectively. The enthalpy and entropy of activation for the disproportionation can be calculated as $H^{\neq} = 26.0$ Kcal/mol and $S^{\neq} = -14.9$ e.u. The lower limit for the rate constant was used because in several much thicker sample specimen (average thickness were not determined), we obtained slower disproportionation rates. We attributed this result to the slow heating rate of the samples.

In conclusion, aside from providing the kinetic information of thiosulfate disproportionation in this paper, we also demonstrated the application of x-ray photoelectron spectroscopy for the study of kinetics of solid phase reactions at high temperatures.

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Acknowledgements

We thank Drs. T. Novakov and R. Dod for helpful discussions and our use of the x-ray photoelectron spectrometer; and Mr. R. Giauque for analyzing the x-ray fluorescence data. This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environment Control Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.

Figure Captions

Figure 1 Sulfur (2p) photoelectron spectra of $Na_2S_2O_3$ at 523°K showing changes in intensity of the reduced sulfur and shift in binding energy of oxidized sulfur as a function of time of heating. a, b, c, d, e and f correspond to 0, 3, 6, 11, 15 and 20 minutes of heating respectively.

Figure 2 A plot of $\ln C_o/C$ as a function of time of heating of $Na_2S_2O_3$ at 498°K.

Figure 3 Temperature dependence of disproportionation rate constant of $Na_2S_2O_3$.

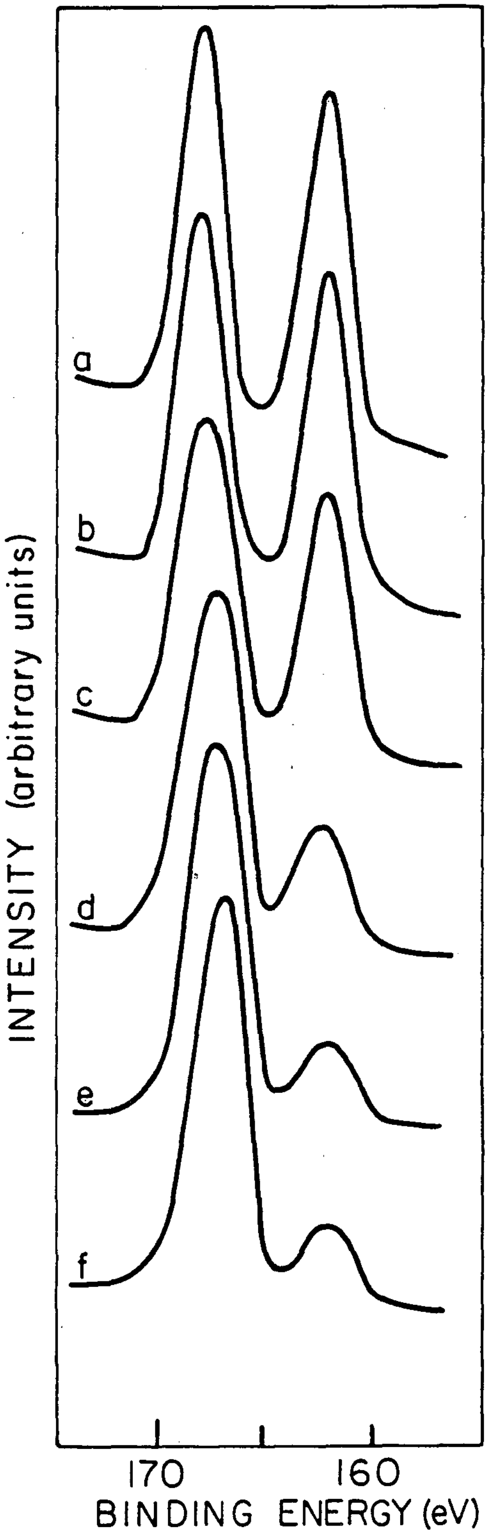

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Figure 1

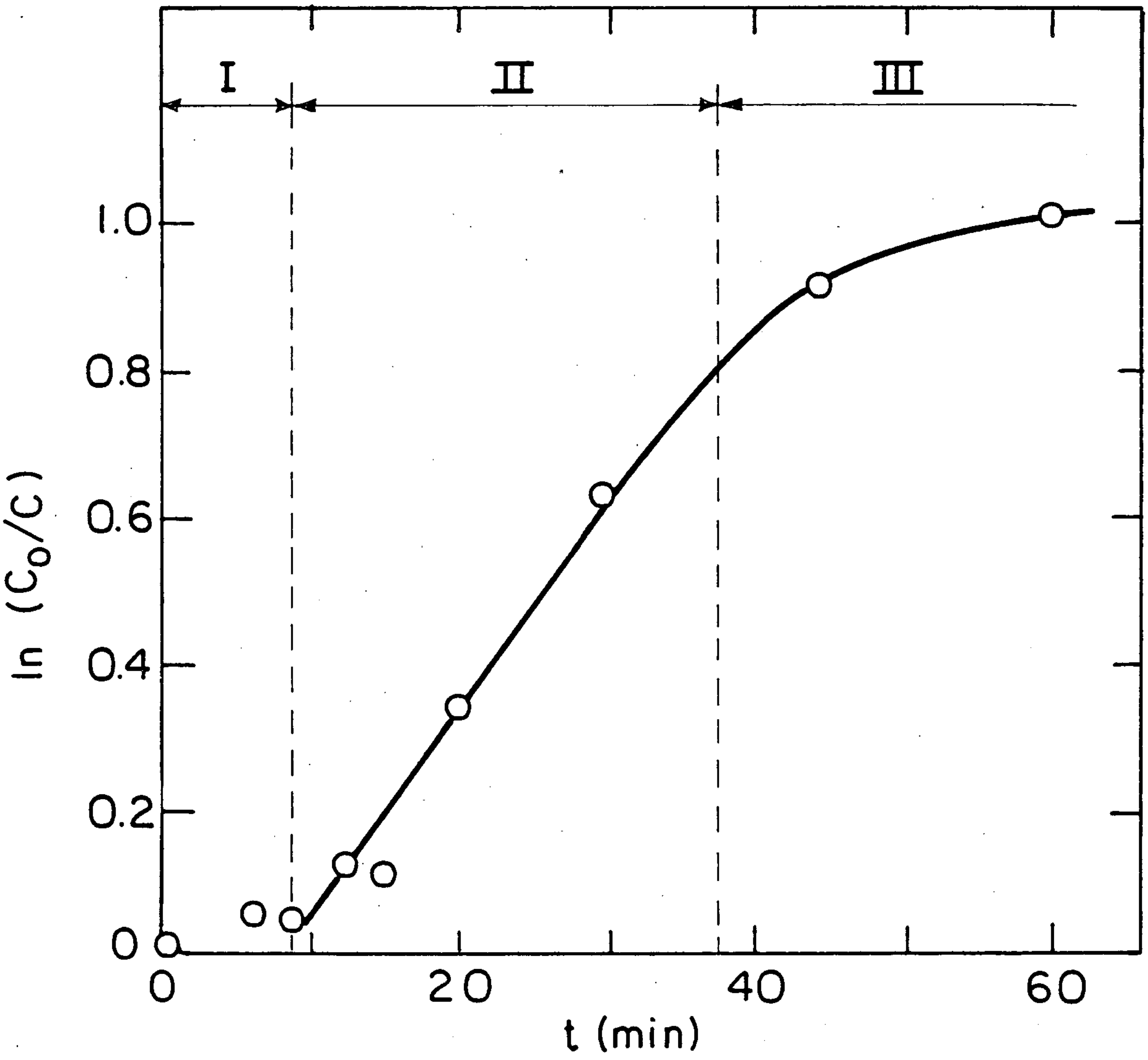

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Figure 2

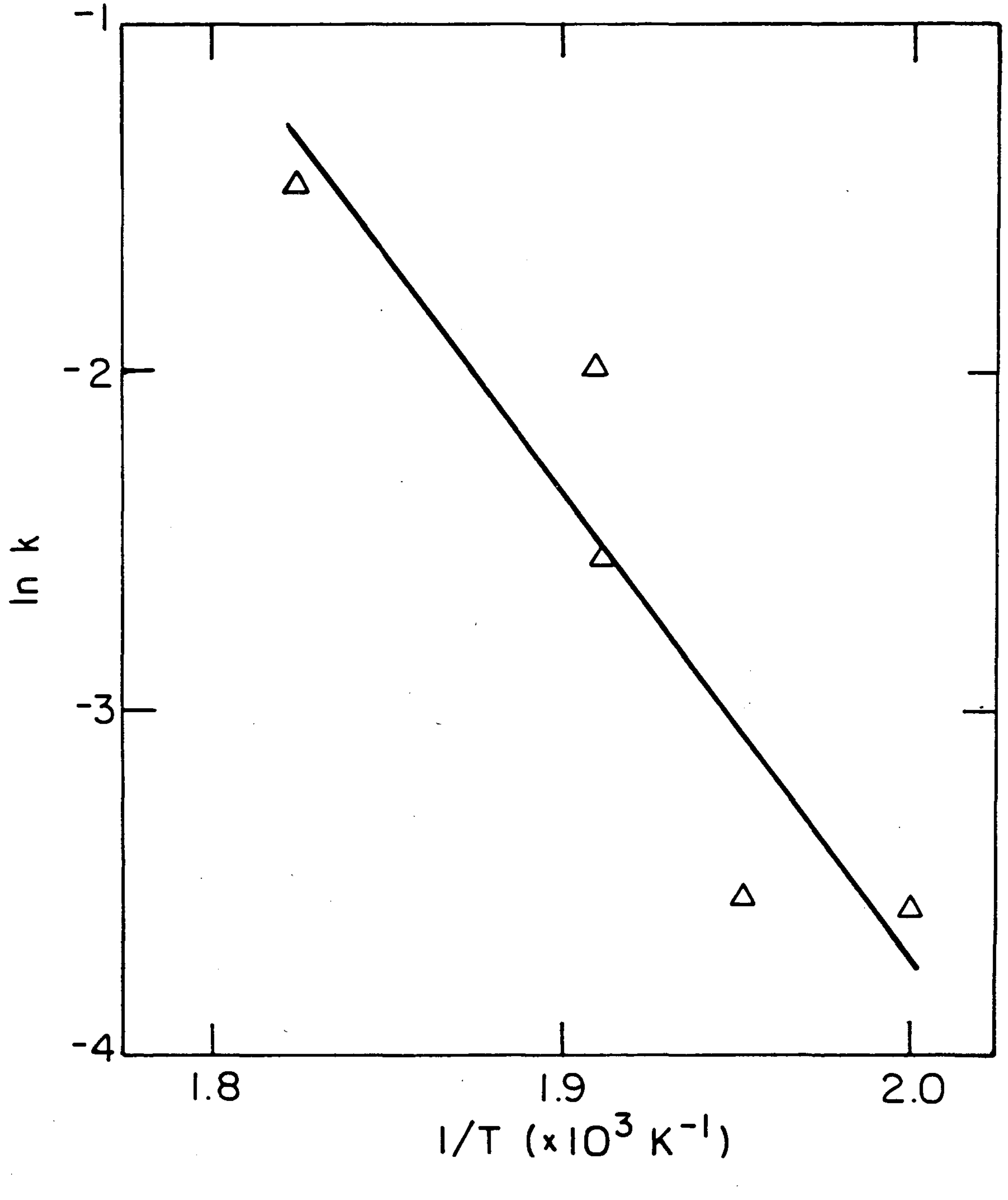

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Figure 3

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