

# Mechanochemical Activation of (SeO<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>) Mixture and Sodium Selenite Synthesis in Vibrational Mill

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**The possibilities of Na<sub>2</sub>SeO<sub>3</sub> mechanochemical synthesis from (SeO<sub>2</sub>+Na<sub>2</sub>CO<sub>3</sub>) stoichiometric mixture were investigated. The experiments were performed using vibrational mill with rings. On the basis of X-ray diffractograms, IR-spectra, and performed chemical analyses, it has been shown that solid state mechanochemical synthesis of sodium selenite was achieved. By the X-ray and IR-spectra analyses, a qualitative determination of the sodium selenite synthesis dynamics was obtained. The structural changes of input compounds occurring during the mechanical treatment and dynamics of these components' consumption during mechanochemical synthesis were investigated. Based on the layout of the kinetics diagram, it was concluded that mechanochemical synthesis of sodium selenite, performed under described conditions, appears to be a zero-order reaction.** © 1998 Academic Press

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## INTRODUCTION

Mechanochemical activation of various inorganic compounds or their mixtures has been studied. During mechanochemical treatment, regardless of applied processing device, the material is comminuted, the size of crystals is reduced, and crystal structure is deformed and damaged, often resulting in partial or complete amorphization (1–3).

A material treated in this way transforms and stores a certain amount of received mechanical energy, thus becoming potentially capable of consuming this energy in different ways (4–6). A significant number of research works have been devoted to the efforts to use such effects of mechanical activation in specific processes, with practical consequences of improved physicochemical characteristics of treated materials (7–9), mechanical alloying of metals (10–12), and mechanochemical preparation of mixed oxides, carbides, and borides (13, 15). If carefully chosen input components are exposed to sufficiently intense mechanical treatment, they may partly or completely react and form new chemical compounds (16–18).

Based on the results of our previous research (19), it is justified to assume that mechanically activated chemical substances will also react with each other in the solid phase

during mechanical activation of binary systems of the type: acid anhydride + alkaline carbonate. So far, mechanochemical synthesis of this type of reacting components has not been investigated.

In order to experimentally test the previous assumption, we investigated the possibility of sodium selenite synthesis by mechanochemical activation of the (SeO<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>) mixture. The main objective of this work was to confirm, on the basis of X-ray, IR spectra, and chemical analyses, that mechanochemical synthesis of sodium selenite from selected starting components is feasible. In this article, the kinetics of sodium selenite mechanochemical synthesis, performed in a vibrational mill with rings, is presented.

## EXPERIMENTAL

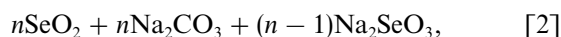
In these experiments, selenium dioxide (min. SeO<sub>2</sub> 98%) and dehydrated sodium carbonate (min. Na<sub>2</sub>CO<sub>3</sub> 99.5%) were used. The substances were produced by Merck AG, pro analysis grade. Mechanochemical activation was performed in a KHD Humboldt Wedag AG vibrational mill, type MH954/3. A stainless steel vessel of 2.5 dm<sup>3</sup> with stainless steel plug and two concentric working rings made of stainless steel were used. The weight of the stainless steel rings was 3.5 kg.

The 100-g samples of (SeO<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>) mixture were prepared from the reactants taken in the stoichiometric ratio appropriate to the expected chemical reaction. The samples were treated for 77 min at a constant regime of 500 RPM, at room temperature (22°C). The samples, taken in seven-minute intervals, were analyzed for the mechanochemical activation effects.

A dependency between synthesis degree and mechanical activation time was examined by standard Schreeters analytical method. This method is based on determination of CO<sub>2</sub> content, i.e., unreacted Na<sub>2</sub>CO<sub>3</sub> in each sample. Having in mind that this reaction proceeds according to the equation,



the samples, taken in seven-minute intervals, would represent the mixture of reacting components and reactional products



where  $0 < n < 1$ . If the sample is treated by diluted HCl in the Schreters vessel, the following reaction will take place:



Developed CO<sub>2</sub> leaves the vessel, causing the equivalent loss of the sample mass. Obviously, the amount of nCO<sub>2</sub> present in the sample indicates the degree of synthesis in the moment of sampling. In other words, the synthesis degree

can be expressed as

$$S = \left[ 1 - \frac{M - N}{0.203 * m} \right] * 100(\%), \quad [4]$$

where  $S$  is the degree of synthesis (in %),  $M$  is total mass of the sample (including vessel and HCl solution) prior to reaction with HCl (g),  $N$  is total mass of the sample after reaction with HCl (g),  $m$  is net mass of the sample (g), and 0.203 is the CO<sub>2</sub> participation factor for the starting mixture. The synthesis level, necessary for the kinetics diagrams, was calculated according to Eq. [4]

Identification of the mechanochemical reaction products was carried out on a Philips PW-1710 automatic diffractometer with a copper tube, operated at 40 kV and 35 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional

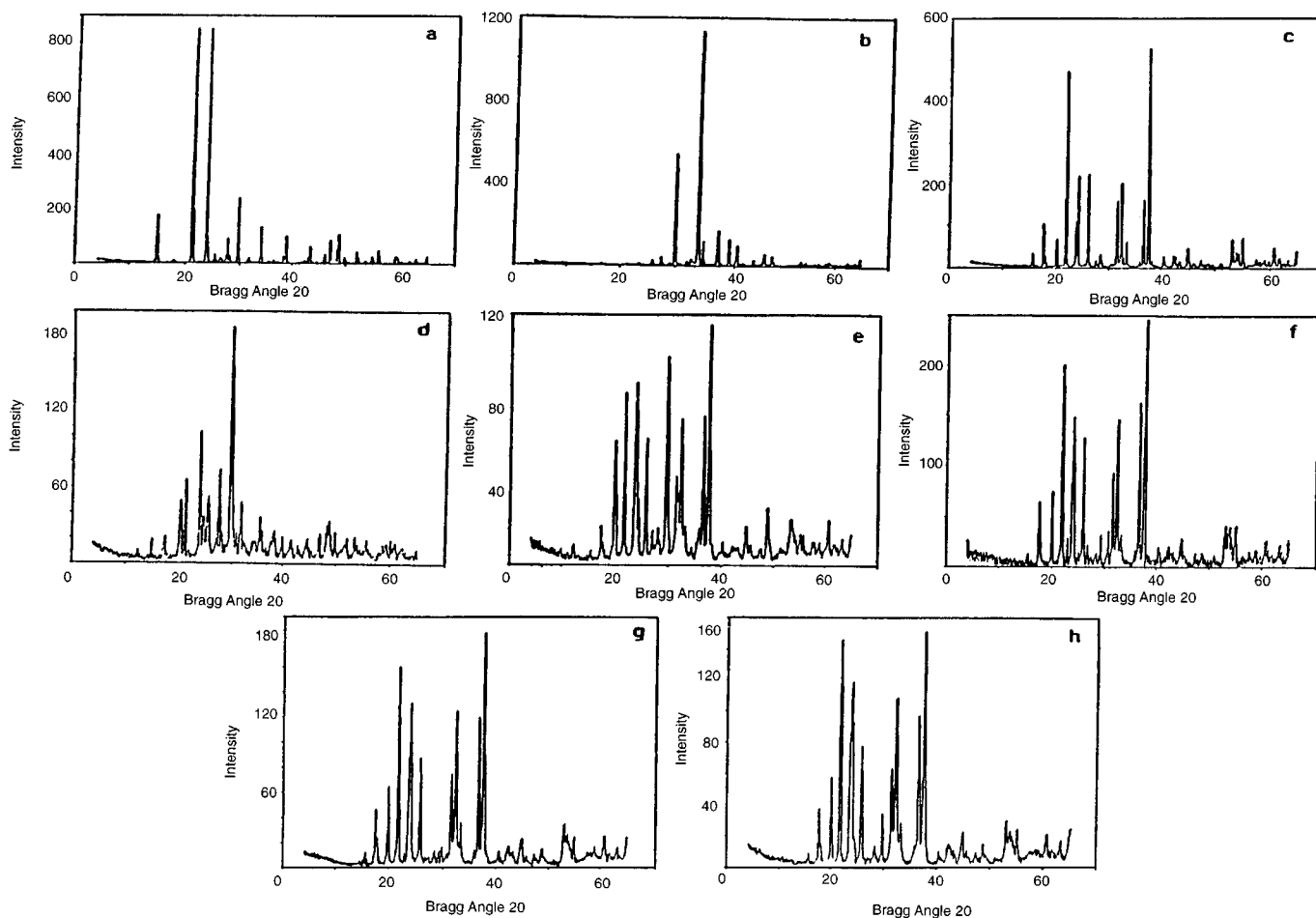


FIG. 1. X-ray diffractograms of pure substances: SeO<sub>2</sub> (a), Na<sub>2</sub>CO<sub>3</sub> (b), Na<sub>2</sub>SeO<sub>3</sub> (c), X-ray diffractograms of mechanochemically activated mixture samples after 7 (d), 28 (e), 42 (f), 56 (g), and 77 (h) min., and X-ray diffractogram of mechanically treated Na<sub>2</sub>CO<sub>3</sub> for 7 min. (i).

counter. Diffraction data were collected in the  $2\theta$  range from  $4^\circ$  to  $15^\circ$ , counting for 2.5 s at each  $0.02^\circ$   $2\theta$  step.

The infrared absorption spectra were obtained on a Perkin-Elmer 782 instrument with a 3600 IR online data station, from  $4000$  to  $400\text{ cm}^{-1}$ , using KBr windows.

## RESULTS AND DISCUSSION

The X-ray diffractograms of the  $(\text{SeO}_2 + \text{Na}_2\text{CO}_3)$  system in various stages of mechanochemical activation are presented in Fig. 1. The arrangement of diffractional maximums and corresponding angles were examined. It can be seen that the diffractogram of the substance mechanochemically activated for 42 min. (Fig. 1f) is identical to the diffractogram of pure sodium selenite (Fig. 1c) (20). Therefore, it can be deduced that synthesis of sodium selenite proceeding during mechanical treatment of the  $(\text{SeO}_2 + \text{Na}_2\text{CO}_3)$  mixture obeys Eq. [1]

The same investigation confirmed that diffractograms of the samples mechanically treated for more than 42 min. (Figs. 1g and 1h) were also identical to the diffractogram of pure sodium selenite. Therefore, reaction [1] occurred within the 42-min. interval.

On the basis of obtained X-ray diffractograms, the reaction dynamics was followed. For this investigation, 12 diffraction angles characteristic of pure sodium selenite were selected. In the diffractograms of mechanically treated samples, the peak intensities at these angles were found to be functionally dependent on the duration of mechanical treatment. Graphic representation of this dependency is presented in Fig. 2a. Both formation and rise of the peak intensities during mechanochemical activation can be easily followed. Almost every one these peak intensities reaches the maximum after 42 min. which corresponds to the diffractogram in Fig. 1f. It can also be seen that in all investigated cases mechanochemical activation beyond 42 min. is followed by intensity decrease. This means that the energy input into the system after 42 min. is spent on destruction of previously formed sodium selenite crystal structure.

The analysis of diffractograms (Fig. 1) enables insight into the structural and phase changes of individual input components. On the basis of the X-ray diffractogram for pure selenium dioxide (Fig. 1a) (20), six diffraction angles bearing the peaks characteristic of this substance were selected. Some of these peaks disappear after only 7 min. of mechanochemical activation. In Fig. 2b, a dependency of the peak intensities on mechanochemical activation time appearing in the diffractograms after 7 min. is presented.

An abrupt decrease of the peak intensities was registered. After 56 min. all characteristic  $\text{SeO}_2$  peaks practically disappear. It can be concluded that immediately after the beginning of mechanochemical activation, the crystal structure of  $\text{SeO}_2$  was substantially damaged and  $\text{SeO}_2$  no longer existed in the mixture as identifiable crystal substance. A similar

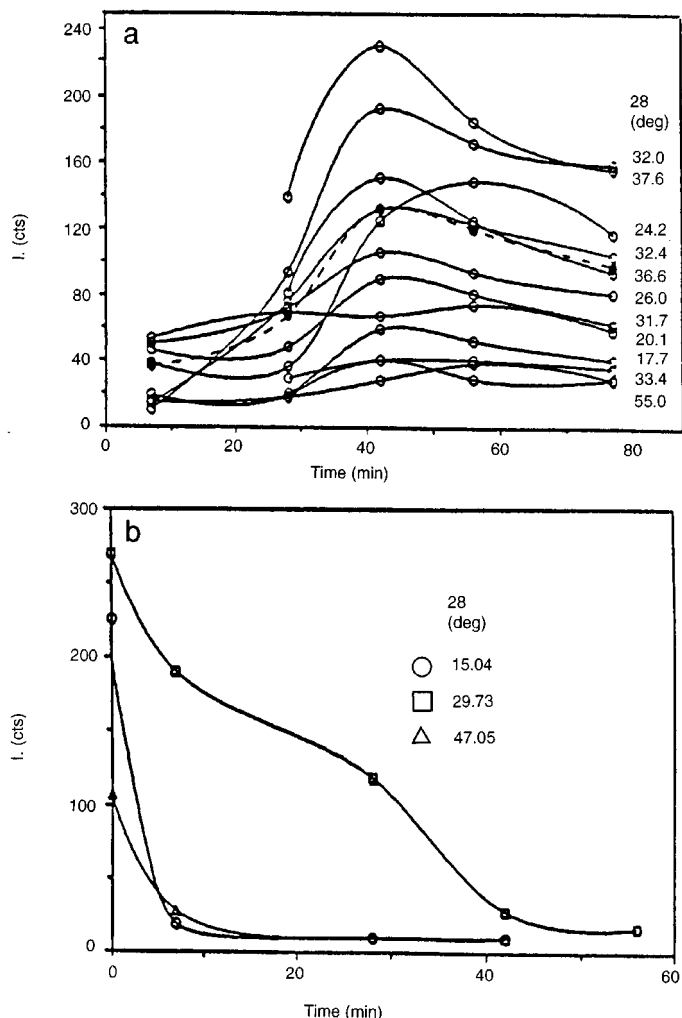


FIG. 2. (a) Intensities of characteristic  $\text{Na}_2\text{SeO}_3$  peaks and their dependency on the mechanochemical activation time. (b) Intensities of characteristic  $\text{SeO}_2$  peaks and their dependency on the mechanochemical activation time.

conclusion can be derived for  $\text{Na}_2\text{CO}_3$ . The sodium carbonate sample was separately treated for five minutes under the same conditions. The X-ray diffractogram for this sample is shown in Fig. 1i. In comparison with untreated sodium carbonate (Fig. 1b) (21), it can be seen that amorphization is almost complete after quite short mechanical treatment.

In Fig. 3, the IR transmission spectra of the mechanically activated samples and the IR spectrum of pure sodium selenite are presented. The spectrum of the sample mechanically treated for only 7 min. records significant effects. Intense vibrations of the  $(\text{SeO}_2^-)$  group can be clearly distinguished at the wave numbers  $850\text{--}700\text{ cm}^{-1}$  and  $540\text{--}430\text{ cm}^{-1}$ . These vibrations are characteristic of sodium selenite (22). Mechanochemical activation beyond 42 min. did not bring any changes in the IR spectra.

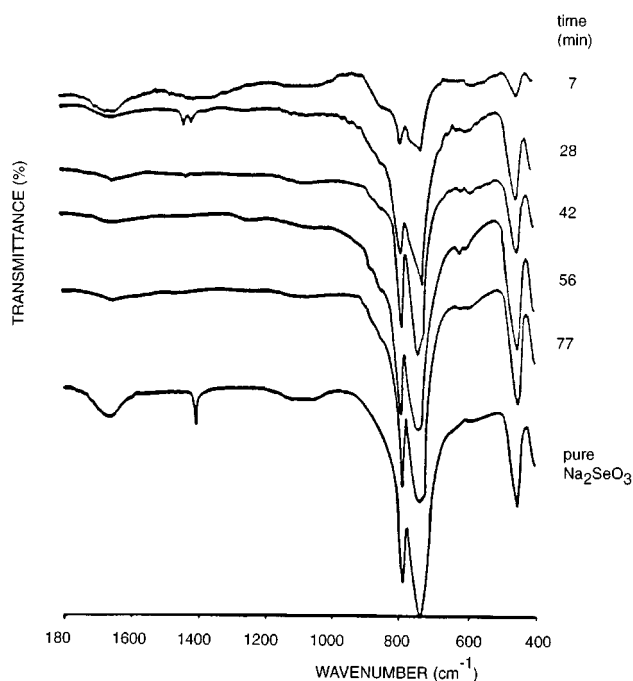


FIG. 3. IR transmission spectra of mechanochemically activated mixture samples and pure Na<sub>2</sub>SeO<sub>3</sub> IR spectrum.

A dependency between the level of synthesis and time of mechanical treatment,  $S = f(t)$ , is presented in Fig. 4.

After 42 min. of mechanical treatment, the achieved degree of synthesis was 95%, i.e., 95% of the input mixture reacted according to Eq. [1]. As can be seen from Fig. 4, the corresponding part of the diagram is represented by a straight line. Such a layout of the kinetics diagram leads us to the conclusion that mechanochemical synthesis of sodium selenite, performed under described conditions, is a typical zero-order reaction. If the reaction rate depended only on the amount of residual reacting components in the reacting mixture, the kinetics diagram would follow the

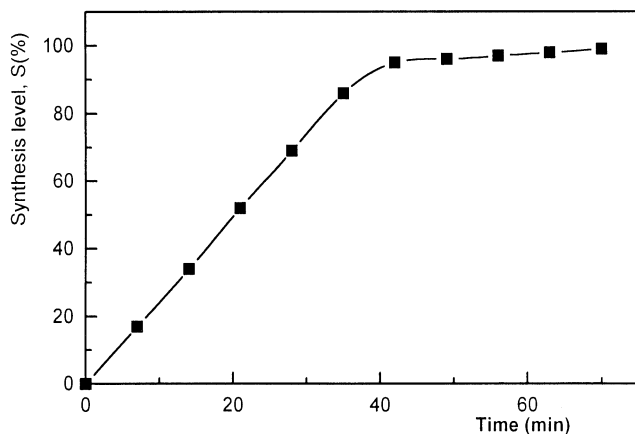


FIG. 4. Graphical representation of kinetics of sodium selenite mechanochemical synthesis.

pattern of the second-order reaction. However, in this case, it seems that numerous parallel-running factors incidentally cancel out to give apparent zero-order kinetics.

From the slope of the straight line section of the kinetics curve, a specific reaction rate constant can be directly obtained. Under described experimental conditions, the rate of reaction [1],  $k = 1.82 \cdot 10^{-4}$  mol/s.

## CONCLUSION

As the results of this work showed, the main effect of mechanochemical activation of a two-component (SeO<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>) mixture was sodium selenite synthesis. By X-ray diffraction, IR spectra, and chemical analyses, the structural and phase changes of input components were studied, and a picture of the formation dynamics of the obtained compound, resulting from mechanochemical activation of the investigated two-component mixture in a vibrational mill, was derived. In our future investigations, the process parameters and influence of the device type will be given particular attention. In addition, the roles of particle size and geometry, change in contact area, degree of agglomeration, and their influences on powder reaction kinetics will be investigated.

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