NOTES *Bull. Chem. Soc. Jpn.*, **56**, *2163—2164 (1983)*

Mechanochemical Decomposition of Dipotassium Peroxodisulfate by Dry Grinding

Itaru Motooka,* Hiroyuki Nariai, and Mitsutomo Tsuhako†

Department of Chemistry, Faculty of General Education, Kobe University, Nada-ku, Kobe 657

†*Kobe Women's College of Pharmacy, Motoyamakitamachi, Higashinada-ku, Kobe 658*

(Received August 2, 1982)

Synopsis. The mechanochemical decomposition of dipotassium peroxodisulfate by dry grinding was investigated by X-ray diffractometry, infrared spectrophotometry, electron spin resonance (ESR) spectrometry, and thermal and volumetric analyses. When dipotassium peroxodisulfate ($K_2S_2O_8$) was ground, type I of $K_2S_2O_8$ was transformed into type II and then into type III. With prolonged grinding, the O–O linkage in $K_2S_2O_8$ was severed to produce $KSO_4\cdot$ radicals, which reacted with a little moisture to give $KHSO_4$.

Mechanochemical phenomena have recently been noted in the wide field of scientific and technical investigations because mechanical treatment influences structures, physical and chemical properties, and reactivity of solids. Although effects of pressure and heat on the mechanochemical phenomena were observed,[1)] mechanical force, particularly shear stress, has an important influence on the scission of chemical bonds.[2)]

The chemical bonds in solid substances are reported to be severed by mechanical treatment[3)] as in the case of grinding sodium pyrophosphate which gives orthophosphates by severing the P–O–P linkage.[4)]

Peroxide is liable to decompose and produce radicals since the O–O bond energy is relatively small. Dipotassium peroxodisulfate gives $SO_4^{-}\cdot$ radicals by heating or exposing to ultraviolet light.[5,6)] Therefore, it is used as an initiator for radical polymerization. If treated mechanically, the O–O bonds in peroxodisulfate are expected to be severed easily to produce radicals such as $SO_4^{-}\cdot$.

In the present paper, the mechanochemical decomposition of dipotassium peroxodisulfate by dry grinding is investigated.

Experimental

Reagent grade dipotassium peroxodisulfate was used without further purification. All other reagents used were of analytical grade.

The X-ray diffraction patterns were obtained with a Rigaku Geigerflex diffractometer using nickel-filtered Cu *Kα* radiation. Infrared spectra were recorded on a JASCO IR-E spectrophotometer equipped with gratings. Thermal analyses (DTA and TG) were carried out by a Rigaku 8002 SD thermal analyzer. The ESR spectra were recorded on a JEOL JES-3BX electron spin resonance spectrometer equipped with an X-band microwave units and 100 kHz field modulation.

The grinding apparatus was an Ishikawa's grinder equipped with an agate mortar and installed in a steel box. Five grams of crystalline dipotassium peroxodisulfate was ground for the specified lengths of time with the relative humidity of 30—40% at room temperature because the mechanochemical effects are affected by the atomosphere, particularly moisture.

The amount of peroxodisulfate ($S_2O_8^{2-}$) was determined volumetrically by adding excess Mohr's salt to a solution of the ground sample and titrating excess iron(II) ion with a standard solution of potassium permanganate. The amount of sulfate (SO_4^{2-}) was determined as follows. Potassium ions in the solution of the ground sample were exchanged for hydrogen ions using a cation-exchange resin. The resulting peroxodisulfuric acid was thoroughly hydrolyzed to sulfuric acid (total sulfate) by heating for 20 min in boiling water, which was titrated with a standard solution of sodium hydroxide. The amount of sulfate in the ground sample was calculated by subtracting the amount of peroxodisulfate from total sulfate.

Results and Discussion

Figure 1 shows X-ray diffraction patterns of $K_2S_2O_8$ at various stages of grinding. The intensity of each diffraction line decreased, the line-width broadened for all the diffraction lines, and the different diffraction lines appeared. That is, with the distortion in crystal lattice, type I of $K_2S_2O_8$ was transformed into type II after a grinding period of 6 h and into type III after 168 h. With further grinding (250 h), the diffraction lines of $KHSO_4$ appeared and became stronger after 430 h. Type I of $K_2S_2O_8$ is apparently converted to $KHSO_4$ through types II and III. The infrared spectra of the samples ground for more than 250 h also indicated the presence of $KHSO_4$.[7)]

Figure 2 shows the DTA and TG diagrams of the ground samples. The DTA and TG curves for 6 and 168 h were essentially the same as those of the original sample. In Fig. 2 an exothermic peak in the 200 °C region with a weight loss is due to the decomposition of $K_2S_2O_8$ with the evolution of oxygen, and the two endothermic peaks at about 330 and 370 °C are due to the order-disorder transformation and melting of $K_2S_2O_7$, respectively.[8)] The melting point lowered with an increase in the grinding time because the particle size became smaller by grinding, and then it coincided in position with the transformation point. The samples ground for 250 h and 430 h also had an endothermic peak at about 200 °C. This peak may be attributed to the pyrolysis of $KHSO_4$ produced by

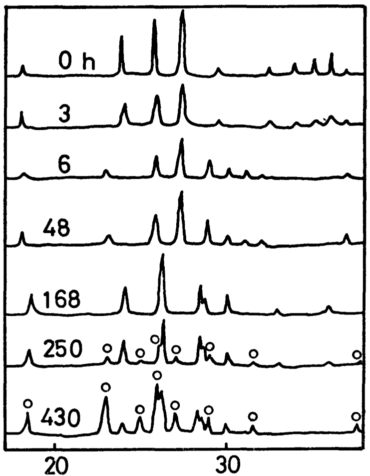

Fig. 1. X-Ray diffraction diagrams of ground samples. ○: $KHSO_4$.

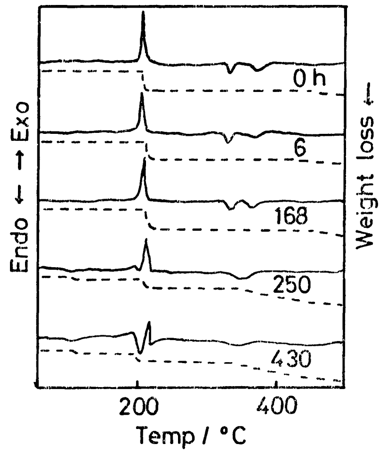

Fig. 2. DTA-TG curves of ground samples. Solid line: DTA, dotted line: TG.

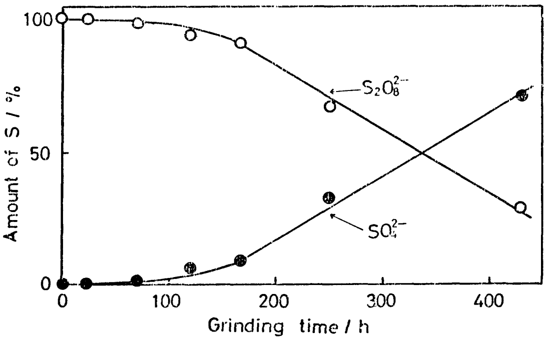

Fig. 3. Changes of distribution of sulfur in ground samples upon grinding.

the grinding of $K_2S_2O_8$. The intensity of this peak increased with an increase in the grinding time, while the weight loss in the 200 °C region decreased. This finding indicates that $K_2S_2O_8$ changes to $KHSO_4$ by grinding. This fact is compatible with the results of X-ray diffractometry and infrared spectrophotometry.

Figure 3 shows the distribution of sulfur in the ground samples. In the first stage of grinding (less than 72 h), sulfate was produced to a small extent and increased with decreasing amount of peroxodisulfate after grinding for more than 120 h.

The absence of peroxomonosulfate (SO_5^{2-}) in the ground samples was confirmed by paper chromatography.[9]

Above findings indicate that $K_2S_2O_8$ decomposes to $KHSO_4$ by prolonged grinding.

Figure 4 shows ESR spectra of the ground $K_2S_2O_8$. A singlet signal with two g values, $g_1=2.011$ and $g_2=2.007$, indicates the presence of radicals, probably $KSO_4\cdot$.[6] In the first stage of grinding, this signal was very weak, reached a maximum in 168 h, and decreased gradually with grinding time. This fact indicates the presence of radicals which are larger in the beginning of the severing of O–O linkages than after grinding for more than 250 h. Thus, it is considered that the radicals produced in the beginning are relatively stable, but that those produced by prolonged grinding react immediately with the moisture adsorbed on the powder surface which is very active due to prolonged grinding.

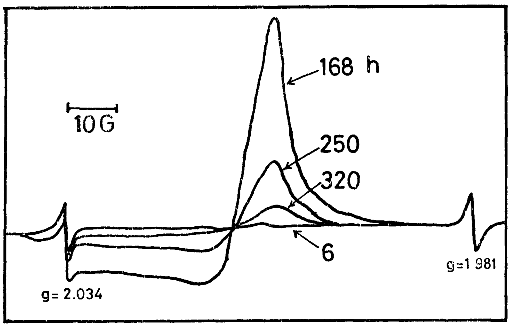

Fig. 4. ESR spectra of ground samples.

It is concluded that the following changes take place when $K_2S_2O_8$ is ground.

$$K_2S_2O_8(\text{type I}) \xrightarrow{\text{Grinding}} K_2S_2O_8(\text{type II}) \xrightarrow{\text{Grinding}}$$
$$K_2S_2O_8(\text{type III}) \xrightarrow{\text{Grinding}} 2KSO_4\cdot \xrightarrow{+H_2O} 2KHSO_4$$
$$+ 1/2\,O_2$$

After conversion I→II→III, the O–O linkages in $K_2S_2O_8$ are severed to produce the $KSO_4\cdot$ radicals which react with a little moisture adsorbed on the powder surface and are stabilized as $KHSO_4$ accompanied by oxygen evolution. The reaction of the $KSO_4\cdot$ radical with H_2O seems to take place by the following mechanism proposed by Kolthoff and Miller.[10]

$$2KSO_4\cdot + H_2O \longrightarrow 2KHSO_4 + 2\cdot OH$$
$$2\cdot OH \longrightarrow H_2O + 1/2\,O_2$$

The authors wish to thank Professor Yukio Kanaji, Faculty of Engineering, Kobe University, for his advice in making the ESR measurements.

References

1) P. S. De Carli and J. C. Jamieson, *J. Chem. Phys.*, **31**, 1674 (1959); F. Dachille and R. Roy, *Nature*, **186**, 34 (1960); Y. Horiguchi, Y. Nomura, and T. Funayama, *Kogyo Kagaku Zasshi*, **68**, 170 (1965); A. C. Greenham and B. P. Richards, *J. Br. Ceram. Soc.*, **69**, 115 (1970).

2) K. Bishof, *Int. Chem. Engr.*, **3**, 80 (1963); H. Takahashi, *Bull. Chem. Soc. Jpn.*, **32**, 235, 381 (1959); H. Takahashi and K. Tsutsumi, "Funtai No Bussei, Kagaku Zokan 31st," ed by K. Iinoya *et al.*, Kagaku Dojin, Kyoto (1967), p. 55; G. Natta and I. Giachetti, *Chim. Ind. (Milan)*, **39**, 1002 (1957); T. Kubo, "Mechanochemistry Gairon," 2nd ed, Tokyo Kagaku Dojin, Tokyo (1978), p. 44; Y. Ogo, N. Nishiguchi, and Y. Okuri, *Bull. Chem. Soc. Jpn.*, **54**, 520 (1981).

3) I. Motooka, G. Hashizume, and M. Kobayashi, *Nippon Kagaku Zasshi*, **87**, 255 (1966); G. Walters *et al.*, *J. Appl. Phys.*, **32**, 1854 (1961); H. Devel *et al.*, *Helv. Chim. Acta*, **39**, 1585 (1956).

4) I. Motooka and M. Kobayashi, "Topics in Phosphorus Chemistry," ed by M. Grayson and E. J. Griffith, John Wiley & Sons, New York (1980), Vol. 10, p. 177.

5) "Kagaku Binran, Oyo-hen," ed by the Chemical Society of Japan, Maruzen, Tokyo (1973), p. 808.

6) P. D. Bartllet and J. D. Cotwan, Jr., *J. Am. Chem. Soc.*, **71**, 1419 (1949); S. B. Barnes and M. C. R. Symons, *J. Chem. Soc., A*, **1966**, 66.

7) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

8) K. D. Cleaver and J. E. D. Davies, *J. Raman Spectrosc.*, **9**, 376, (1980).

9) Peroxophosphate (PO_5^{3-}) was found to be present when tetrapotassium peroxodiphosphate was ground (unpublished data).

10) I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).