

- 1983, 105, 5786.
6. (a) VanAtta, R. B.; Franklin, C. C.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 4121. (b) Franklin, C. C.; VanAtta, R. B.; Tai, A. F.; Valentine, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 814.
 7. (a) Suga, A.; Sugiyama, T.; Otsuka, M.; Ohno, M.; Sugiura, Y.; Maeda, K. *Tetrahedron* **1991**, *47*, 1191. (b) Kimura, E.; Shionoya, M.; Yamauchi, T.; Shiro, M. *Chem. Lett.* **1991**, 1217. (c) Hill, C. L.; Brown, R. B.; Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. (d) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.
 8. (a) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 1772. (b) Bressan, M.; Morvillo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 650. (c) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908. (d) Koola, J. D.; Kochi, J. K. *J. Org. Chem.* **1987**, *52*, 4545. (e) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
 9. Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6377.
 10. (a) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 4977. (b) Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 7826. (c) Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7195.
 11. (a) Tai, A. F.; Margerum, L. D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006. (b) Margerum, L. D.; Liao, K. I.; Valentine, J. S. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372, American Chemical Society: Washington, DC, U. S. A., 1988; pp 105-115. (c) Valentine, J. S.; VanAtta, R. B.; Margerum, L. D.; Yang, Y. In *Activation of Dioxygen and Homogeneous Catalytic Oxidations*; Ando, W., Ed.; Elsevier: New York, U. S. A., 1988; pp 175-184.
 12. (a) Valentine, J. S.; Nam, W.; Ho, R. Y. N. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R.; Martell, A. E.; Sawyer, D., Eds.; Plenum: New York, U. S. A., 1993; pp 183-198. (b) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2986. (c) Kinnerary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124. (d) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110*, 1953. (e) Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967. (f) Lindsay Smith, J. R.; Sleath, P. R. *J. Chem. Soc. Perkin Trans. 2* **1982**, 1009. (g) Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231.
 13. (a) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121. (b) Sorrel, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250.
 14. Kinneary, J. F.; Wagler, T. R.; Burrows, C. J. *Tetrahedron Lett.* **1988**, *29*, 877.
 15. (a) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* **1990**, *29*, 357. (b) Ghosh, P.; Tyeklar, Z.; Karlin, K. D.; Jacobson, R. R.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 6889. (c) Karlin, K. D.; Cruse, R. W.; Gultneh, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 599.
 16. (a) Arasasingham, R. D.; He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 7985. (b) Garrison, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 191. (c) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.
 17. VanAtta, R. B. Ph.D. Dissertation, University of California, Los Angeles, 1987.
 18. *Organic Synthesis*; Saltzman, H.; Sharefkin, J. G., Eds.; Wiley: New York, U. S. A., 1973; Collect. Vol. V, pp 658-659.
 19. Chapman, D. R.; Reed, C. A. *Tetrahedron Lett.* **1988**, *29*, 3033.
 20. Kanda, W.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3268.

Chemistry of Carbonate-Sulfur Flux

Q. Won Choi, Han Choi, So-Young Chang, Chong-Hong Pyun, and Chang-Hong Kim*

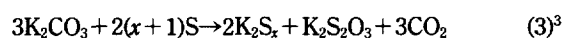
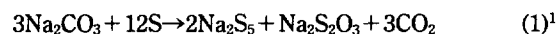
Division of Applied Science, Korea Institute of Science and Technology, P.O. Box 131, Seoul 130-650, Korea

Received September 8, 1994

Reactions of alkaline metal carbonates with sulfur are investigated in detail. The evolution of CO and a trace of SO₂ were observed in the course of reaction with major component of polysulfides. Some evidences that the reaction proceeds with breaking of terminal sulfur-sulfur bond in the sulfur polymer, and forming CO, SO₂ and polysulfide are presented. Polysulfides have the role of keeping free sulfur and allow it to react with other chemicals to rather high temperatures.

Introduction

The reaction of alkaline metal carbonate and sulfur has been known to produce alkaline metal polysulfides.



*To whom correspondence should be addressed.

(the reaction of Na₂CO₃ with S begins at 275-280 °C; that

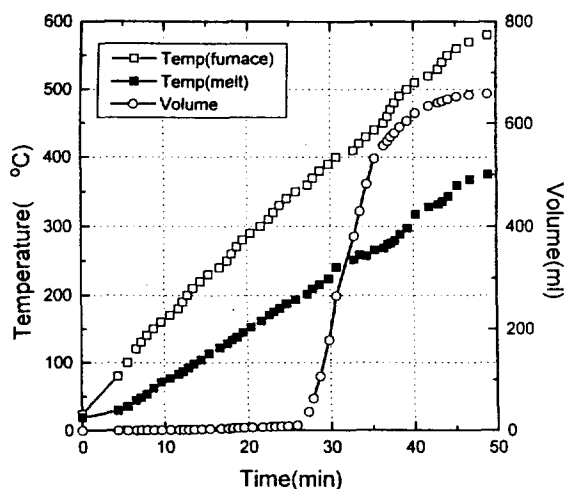
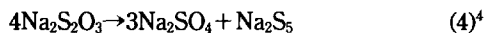


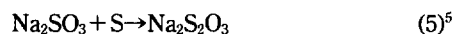
Figure 1. Gas evolution for the reaction of Na_2CO_3 and S. The composition of the reactants: Na_2CO_3 , 0.03 mole; S, 0.1 mole.

of K_2CO_3 with S begins at 108°C and completes below 180°C

On the other hand, sodium thiosulfate disproportionates at temperatures above 223°C as



and is formed readily at lower temperatures by the reaction



Alkaline metal carbonate-sulfur flux was used for preparing sodium chromium sulfide (NaCrS_2) from NaCrO_2 or Cr_2O_3 .⁶ Recently yttrium oxysulfide ($\text{Y}_2\text{O}_2\text{S}$) has been prepared in the same flux.⁷

In the present work, further details of reactions taking place in the alkaline metal carbonate-sulfur flux have been studied.

Experimentals

All of the chemicals used in this investigation were from commercial products of chemical pure grade without further purification.

The reaction mixture was loaded in a quartz tube and heated in an electric furnace. The gaseous products were collected above water in a Mariott bottle, to measure volume and to sample for IR spectral analysis.

The molten mass remaining in the quartz tube was washed out with water and analyzed for anions in it: Water soluble sulfides, sulfites, and thiosulfates of the reaction products were analyzed by iodometry, and sulfates by conductometry with barium chloride. Water insoluble solids were analyzed by XRD and IR.

Results and Discussion

Reaction of Na_2CO_3 with S. Gas evolution is represented in Figure 1. IR spectra shown in Figure 2 reveal that the gaseous product is mainly CO_2 and a small amount of COS, indicating production of CO gas in the course of

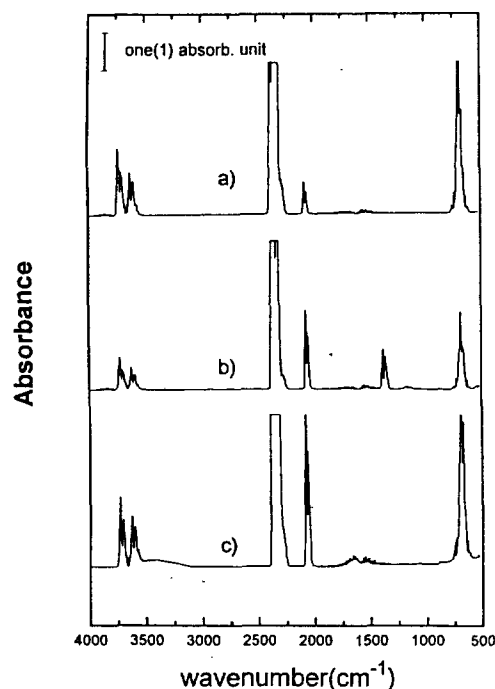
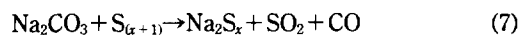


Figure 2. Infrared spectra of evolved gas for the reaction of: a) Na_2CO_3 (0.09 mole) and S (0.22 mole), and gas is collected at temperatures from room temperature to 470°C ; b) CaCO_3 (0.001 mole), Na_2CO_3 (0.0015 mole) and S (0.01 mole), and gas is collected at temperatures from 450°C to 650°C ; c) CaCO_3 (0.04 mole) and $\text{Na}_2\text{S}_2\text{O}_3$ (0.08 mole), and gas is collected at temperatures from 500°C to 600°C .

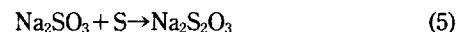
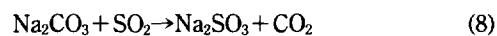
reaction. Since $\text{CO} + \text{CO}_2$ mixture of total pressure 1 atm can contain less than 0.1% CO below 400°C due to the Bourdour reaction



Since the reaction (6) is rather slow at lower temperatures, most of CO would be converted to $\text{C} + \text{CO}_2$ and small amount of CO may react with sulfur to form COS. The volume of gas evolved corresponds to 0.8 mole per mole of sodium carbonate used. Therefore, it is plausible to assume the reaction proceeds as follows:

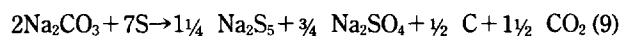


followed by the reaction (7),



followed by the reaction (4).

Overall reaction can be described as



which would predict that 1.5 mole of CO_2 will be produced from 2 moles of Na_2CO_3 , but part of CO from reaction (7) would be followed as:



Actual total gas volume was measured to 1.61 mole, corresponding to conversion of 20% of CO to COS.

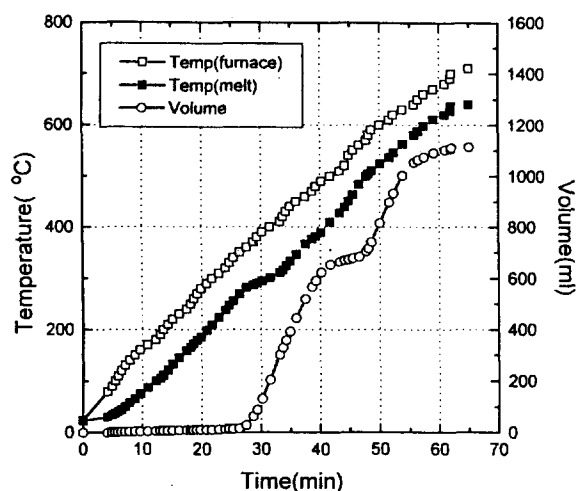
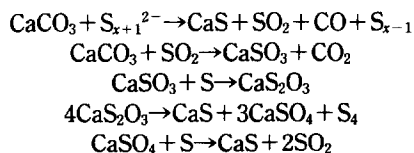


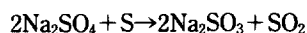
Figure 3. Gas evolution for the reaction of CaCO_3 , Na_2CO_3 and S. The composition of the reactants: CaCO_3 , 0.02 mole; Na_2CO_3 , 0.03 mole; S, 0.1 mole.

Gas evolution starts at about 300 °C and is completed at around 400 °C.

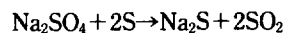
Reaction of CaCO_3 with Na_2CO_3 and S. The course of reaction for this mixture is shown in Figure 3, which indicates that CaCO_3 reacts with sulfur after completion of $\text{Na}_2\text{CO}_3 + \text{S}$ reaction, from about 450 °C. The IR spectra indicates the gaseous product is constituted mainly of CO_2 with a fair amount of COS and small amount of SO_2 . The volume of gas produced at each step corresponds to nearly 3/4 moles per mole of metal carbonate present; the first stage: 0.81 mole per mole of Na_2CO_3 , the second stage: 0.89 mole per mole of CaCO_3 . Therefore, the reaction mechanism for $\text{CaCO}_3 + \text{S}$ reaction appears to be the same as for Na_2CO_3 . The differences of this reaction with the previous sodium carbonate reaction are that CO is produced at higher temperature, so COS formation proceeds faster and that greater stability of solid CaS may prevent formation of calcium polysulfides.



Furthermore, the reaction



takes place below 550 °C. At temperature above 600 °C, the reaction



may be predominant, but supply of free sulfur from the flux will become negligible at higher temperatures. In fact, gaseous product obtained beyond 550 °C does not contain detectable amount of SO_2 .

Reaction of Na_2CO_3 with $\text{Na}_2\text{S}_2\text{O}_3$. The total amount of gaseous product evolved corresponds to 0.31 mole per $\text{Na}_2\text{S}_2\text{O}_3$ used. Gas evolution starts at 420 °C and ends at about 600 °C (Figure 4). Since 1 mole of free sulfur as Na_2S_5 is produced by disproportionation reaction (4) from 4 moles

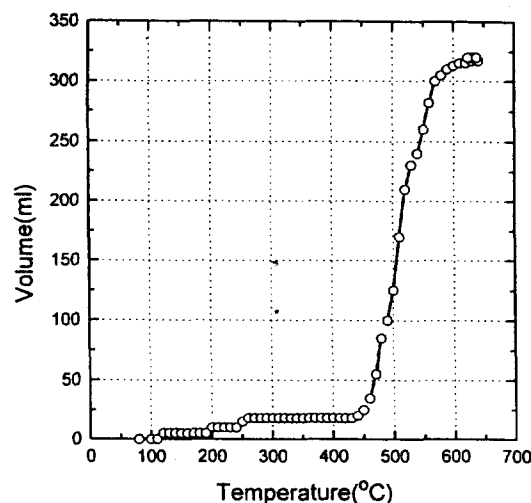


Figure 4. Gas evolution for the reaction of Na_2CO_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The composition of the reactants: Na_2CO_3 , 0.04 mole; $\text{Na}_2\text{S}_2\text{O}_3$, 0.04 mole.

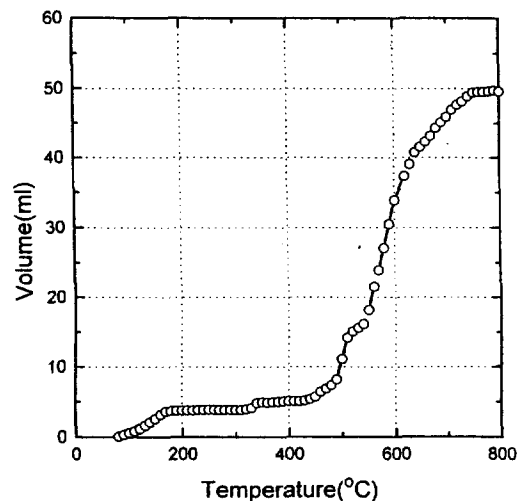


Figure 5. Gas evolution for the reaction of CaCO_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The composition of the reactants: CaCO_3 , 0.002 mole; $\text{Na}_2\text{S}_2\text{O}_3$, 0.005 mole.

of $\text{Na}_2\text{S}_2\text{O}_3$, more than 0.25 mole of CO_2 per mole of $\text{Na}_2\text{S}_2\text{O}_3$ is expected to be produced assuming the disproportionation reaction (4) and decomposition of $\text{Na}_2\text{S}_2\text{O}_3$. When $\text{Na}_2\text{S}_2\text{O}_3$ alone is heated small amount of SO_2 evolves up to 600 °C.

Reaction of CaCO_3 with $\text{Na}_2\text{S}_2\text{O}_3$. The gas evolution starts at about 475 °C and ends at about 800 °C. The volume of gas produced is about 0.32 mole per mole of $\text{Na}_2\text{S}_2\text{O}_3$ used (Figure 5). From Figure 3 and 4, supply of free sulfur by the disproportionation reaction (4) of sodium thiosulfate is fast enough for $\text{CaCO}_3 + \text{S}$ reaction at about 450 °C.

Reaction of Na_2S with Y_2O_3 . It has been known that $\text{Y}_2\text{O}_2\text{S}$ can be prepared by the reaction of Y_2O_3 in $\text{Na}_2\text{CO}_3 + \text{S}$ flux (starts at 375 °C⁸), but the reaction of Na_2S with Y_2O_3 did not lead to formation of $\text{Y}_2\text{O}_2\text{S}$. The reaction of Y_2O_3 in $\text{Na}_2\text{CO}_3 + \text{S}$ flux is very complex and the detailed reaction will be presented in a later paper.

Reaction of CaCO_3 with Na_2S . no reaction was ob-

served.

Conclusion

In conclusion, the carbonates may be assumed to attack the terminal sulfur-sulfur bond in the sulfur polymer to form CO, SO₂ and sulfide, and leaving free sulfur chain to form polysulfide with sulfide. Thus, the role of Na₂CO₃+S flux is to keep free sulfur in the form of sodium polysulfide allowing the latter to react with other chemicals up to rather high temperature⁹. In case of carbonates reacting at higher temperatures, COS may also contribute to sulfurization reactions.

References

1. Fordos, M.-J.; Gelis, A. *Ann. Chim. Phys.* **1846**, 3(18), 86;
2. Berthelot, M. C. *r.* **1883**, 96, 298.
3. Kanatzidis, M. G. *Chem. Mater.* **1990**, 2, 357.
4. Brückner, K. *Ber. Wien. Akad.* **1905**, 114 IIa, 1157; *Monatsh.* **1906**, 27, 49.
5. Wyszinski, C. *Przegląd Chem.* **1938**, 2, 552.
6. Schneider, R. *J. prakt. Chem.* **1873**, 8, 38; **1897**, 56, 415.
7. Royce, M. R.; Smith, A. L.; Thomsen, S. M.; Yocom, P. N. *The Electrochemical Soc. Extended Abstracts* Vol. 69-1, May 4-9, 1969, Abstract 86, p 201.
8. Mho, S.-I.; Chang, S.-Y.; Jeon, C.-I.; Pyun, C.-H.; Choi, Q.-W.; Kim, C.-H. *Bull. Korean Chem. Soc.* **1990**, 11, 386.
9. Pearson, T. G.; Robinson, P. L. *J. Chem. Soc.* **1930**, 1473 or *Phase Diagrams for Ceramists*; The American Ceramic Society, 1983; Vol. V, p 273.