Mechanism for Forming Sodium Pyrosulfate from Sodium Chloride, Sulfur Dioxide, and Oxygen

Alfred B. Anderson* and S. C. Hung

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. *Received May 12, 1983*

Abstract: Energy and reaction pathway calculations show sodium pyrosulfate ($Na_2S_2O_7$) is more stable than sodium sulfate (Na_2SO_4) + SO_3(g). A common precursor to both products when formed on a NaCl surface is an $SO_2 + O_2$ adduct which transfers an oxygen atom to SO_3. A low-energy barrier to this process is reached as the O_2 bond stretches and two electrons are transferred from chloride in the surface, yielding trigonal-pyramidal SO_4^{2-} which has two paths open to it. The lower-energy path has this SO_4^{2-} bond to SO_3 leading to pyrosulfate; the higher-energy path has this SO_4^{2-} take the tetrahedral sulfate structure. Cl_2 leaves the surface after the pyrosulfate or sulfate forms. Na^+ leaves the surface to bond to the anions. Both anions undergo low activation energy umbrella distortions, yielding tetrahedrally coordinated S. Our results offer strong theoretical support for the experimental results of Fielder, Stearns, and Kohl: specifically, (a) rate is proportional to SO_3 pressure; (b) $Na_2S_2O_7$ forms first at lower temperatures; (c) $Na_2S_2O_7$ decomposes, generating Na_2SO_4; and (d) Na_2SO_4 forms directly at higher temperature. At high temperatures the $T\Delta S$ contribution is larger than the ΔH contribution to ΔG, favoring sulfate formation even though it has a greater enthalpy than pyrosulfate at low temperatures.

In a recent study Anderson and Debnath[1] used molecular orbital theory to determine a low-energy pathway for sodium sulfate formation from sodium chloride, oxygen, and sulfur dioxide according to the reaction

$$2NaCl(s) + O_2(g) + SO_2(g) + SO_3(g) \rightarrow Na_2SO_4(s) + Cl_2(g) + SO_3(g) \quad (1)$$

In this reaction SO_3 acts as a catalyst, reacting with a previously studied[2,3] singlet $SO_2{\cdot}O_2$ adduct near the NaCl surface to abstract O, forming SO_4 which accepts two electrons and 2 Na^+ from the surface, to yield Na_2SO_4. The other products are SO_3 and Cl_2. A first-order dependence on catalyst (SO_3) concentration and a low 22-kJ/mol reaction barrier determined experimentally by Fielder et al.[4] lend support to the predicted mechanism.

Recent experimental investigations of Kohl et al.[5] show sodium sulfate is not the only possible product. While from 450 to 625 °C Na_2SO_4 is the dominant product, at lower temperatures, 400 to 450 °C, sodium pyrosulfate, $Na_2S_2O_7$, forms in the molten state. The pyrosulfate anion, $S_2O_7^{2-}$, is of the form of a symmetric $SO_4^{2-} + SO_3$ adduct which is presumably driven to loss of SO_3(g) at higher temperatures due to the entropy increase and its effect on ΔG through the $T\Delta S$ contribution (ΔH is obviously positive for the loss process). This new information would appear to be readily explained by a mechanism where at the transition state for reaction 1, $(O_2SO\cdots OSO_3)^{2-}$, the O joining SO_3 carries SO_3 with it and bonds to the S of the newly-formed SO_3. This mechanism is the theme of this study. The same atom superposition and electron delocalization molecular orbital (ASED-MO) theory and the same parameters as in ref 1 are used here.

Sodium sulfate formation under the conditions described above has technological importance. Liquid sodium sulfate forms according to reaction 1 on metal alloy turbine blades where it is a powerful corrosive agent,[6] capable of destroying protective oxide layers, leading to failure by "hot corrosion".[7] Sulfates and pyrosulfates are also important to sulfuric acid formation.

Results and Discussion

When the C_s $SO_2{\cdot}O_2$ adduct forms on the surface it is easily bent to the C_1 structure in Figure 1 so that it can react with SO_3 as shown. In ref 1 calculations were performed up to the transition state for O–O bond breaking on a cluster surface model. As shown there, when the O–O bond stretches to the transition state an O_2 Π^* orbital drops low enough in energy to accept electrons from chloride anions in the surface. At this point 2 Na^+ cations join the trigonal-pyramidal SO_4^{2-} anion and Cl_2(g) leaves the surface. For simplicity, we omitted the surface cluster at this point. The completion of the reaction leading to a tetrahedral SO_4^{2-} anion and SO_3(g) is shown in the right-hand pathway of Figure 1.

In the present study we have calculated the reaction surface for an alternate reaction shown in the left-hand pathway of Figure 1. The precursor to the transition state has two eclipsed SO_3 fragments joined to the connecting O with Na^+ anions placed as shown. For $Na_2S_2O_7$, the transition to the final tetrahedral coordination involves a small barrier of 18 kJ/mol compared to 33 kJ/mol for SO_4^{2-}. Our (approximate) calculations have the reaction

$$Na_2S_2O_7(g) \rightarrow Na_2SO_4(g) + SO_3(g) \quad (2)$$

endothermic by 169 kJ/mol.

Sodium pyrosulfate formation was also studied with SO_3 fragments at each end staggered. In this case the precursor, transition state, and product were only slightly less stable by the respective amounts 8, 9, and 4 kJ/mol. The structure of $Na_2S_2O_7$ does not seem to be known experimentally, but an X-ray determination by Lyton and Truter for crystalline $K_2S_2O_7$[8] agrees with the eclipsed conformation favored by our calculation. We have assumed a tetrahedral S coordination for simplicity and Lyton and Truter find angles varying from 101.3 to 115.5° (109.5° is the tetrahedral angle). We fixed the three S–O bond lengths at each end to the same value, optimized to be 1.49 Å compared to Lyton and Truter's range of 1.428 to 1.447 Å. Larger differences are found in comparing our calculated inner bridging S–O bond lengths of 1.46 Å and the S–O–S angle of 144° with the Lyton and Truter values of 1.645 Å and 124.2°. Presumably our approximate non-self-consistent theory is letting the SO_3 fragments with their negative charges get too close together (the central O is nearly neutral). The angle is dependent on these two bond lengths; when they are set to 1.645 Å, the optimal angle is cal-

(1) A. B. Anderson and N. C. Debnath, *J. Phys. Chem.*, **87**, 1938 (1983).
(2) A. B. Anderson, *Chem. Phys. Lett.*, **93**, 538 (1982).
(3) R. Kugel and H. J. Taube, *J. Phys. Chem.*, **79**, 2130 (1975).
(4) W. L. Fielder, C. A. Stearns, F. J. Kohl, and G. C. Fryburg, "Formation of Na_2SO_4(c) from NaCl(c), SO_2(g) and O_2(g)", International Conference on High-Temperature Corrosion, San Diego, CA, March 2–6, 1981.
(5) F. J. Kohl and W. L. Fielder, private communication.
(6) G. C. Fryburg, F. J. Kohl, C. A. Stearns, and W. L. Fielder, *J. Electrochem. Soc.*, **129**, 571 (1982).
(7) J. Stringer, *Annu. Rev. Mater. Sci.*, **7**, 477 (1977).
(8) H. Lyton and M. R. Truter, *J. Chem. Soc., Part 4*, 5112 (1960).

0002-7863/83/1505-7541$01.50/0

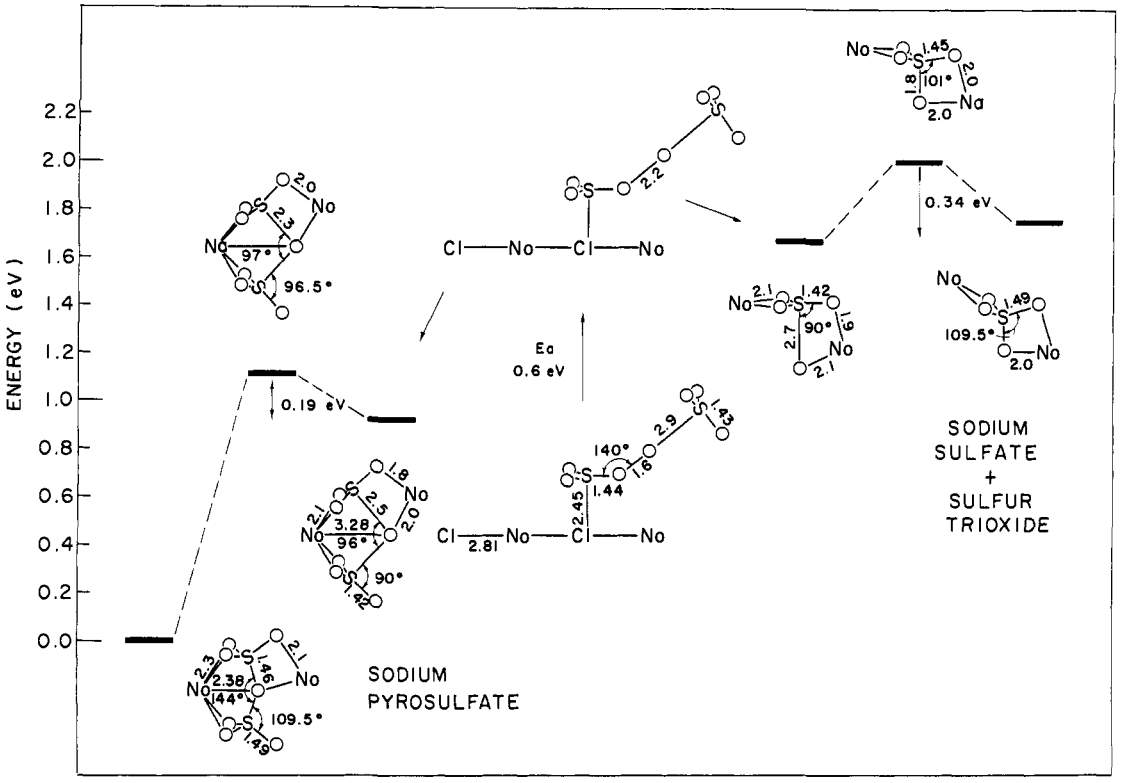

Figure 1. The central section shows SO_3 interacting with SO_2-O_2 adduct on the NaCl surface going to the transition state. After the transition state Cl_2 and the surface are omitted for simplicity. The energetics and mechanism for $Na_2SO_4 + SO_3$ formation are on the right. $Na_2S_2O_7$ formation is shown to the left.

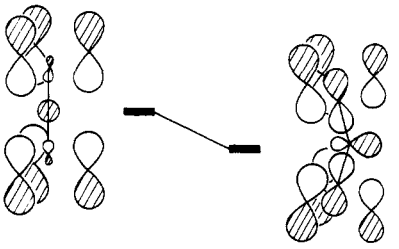

Figure 2. Orbital stabilization predominantly responsible for the bent S–O–S bond in the pyrosulfate anion.

culated to be 123.5°, agreeing with experiment for solid $K_2S_2O_7$.

The S–O–S bonding is a consequence of a single orbital becoming stabilized as in Figure 2. On each SO_3 end the $1a_2''$ Π orbital (ref 1) may be seen to be antibonding to an s orbital on the central O when S–O–S is linear. On bending there is s–p hybridization on the central O, allowing bonding stabilization between it and the two S atoms. This effect is stronger than the usual Milliken–Walsh explanation of the cause of bending in H_2O where the $2a_1$ lone-pair orbital is stabilized on bending.[9]

In solid potassium pyrosulfate the anions are shared among cations so it is unlikely that a detailed comparison can be made with cation positions in our sodium pyrosulfate molecule. A general feature may, however, be noted: In $K_2S_2O_7$(s) the cations are closely associated with nine oxygens of four anions. In $Na_2S_2O_7$(g) we find one Na^+ is associated with five oxygens and the other with two oxygens. In the staggered form, one Na^+ is associated with four oxygens and the other with three. Thus the cations want to get as close as they can to the anions for strongest bonding.

The molecular orbital analysis of the anion–cation bonding is shown for sodium sulfate in Figure 3. Two sulfate *a* symmetry orbitals are significantly stabilized by overlap with Na s orbitals. The lower-orbital stabilization involves a negative overlap, which has been seen in a variety of other studies as well,[10-12] and which

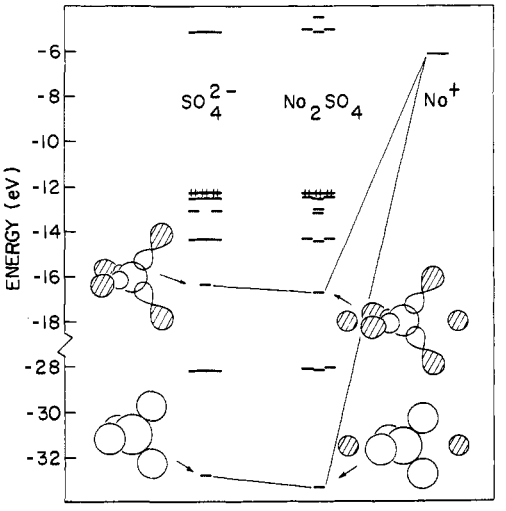

Figure 3. Bonding stabilizations between Na^+ cations and SO_4^{2-} anion.

Whangbo and Hoffmann have explained by using the perturbation theory.[11] The upper involves in-phase stabilization. It is reasonable that the most stabilization will be gained in pyrosulfates as well when the cation s orbitals interact with as many constituent atoms in the anion as possible.

We see (Figure 1) that $Na_2S_2O_7$(g) is energetically more stable than Na_2SO_4(g) + SO_3(g), which is consistent with experiments showing the pyrosulfate forms at 400–450 °C.[5] The conversion to sulfate and SO_3(g) in the 450–625 °C range may be understood by appealing to ΔS for the reaction

$$Na_2S_2O_7(l) \rightarrow Na_2SO_4(l) + SO_3(g) \qquad (3)$$

When $\Delta G = \Delta H - T\Delta S$ is negative, the above reaction will proceed to the right. A thermal decomposition study of Kostin et al.[13]

(9) See, for example, B. M. Gimarc, *J. Am. Chem. Soc.*, **93**, 593 (1971).

(10) A. B. Anderson, *J. Catal.*, **67**, 129 (1981).
(11) M.-H. Whangbo and R. Hoffmann, *J. Chem. Phys.*, **68**, 5498 (1978).
(12) C. J. Marsden and L. S. Bartell, *Inorg. Chem.*, **15**, 2713 (1976).

indicates $\Delta H°$ is 144 kJ/mol for reaction 3, quite close to our calculated value of 169 kJ/mol for the gas-phase reaction 2. They find, furthermore, a value of 139 J/deg·mol for $\Delta S°$.

Conclusion

Using molecular orbital theory, we have determined reaction mechanisms for sodium sulfate and sodium pyrosulfate formation from solid sodium chloride, sulfur dioxide, and oxygen. The reaction involves a singlet $SO_2 \cdot O_2$ intermediate adsorbed to the NaCl surface. Gas-phase SO_3 abstracts an oxygen atom from O_2 in the $SO_2 \cdot O_2$ adduct, forming SO_4^{2-}. As this anion forms Na^+ cations from the surface bond to it and $Cl_2(g)$ desorbs. The anion has two pathways open to it; the lower-energy one has it bonding to the SO_3 left behind on the surface, forming $S_2O_7^{2-}$. Both the sulfate and pyrosulfate precursors undergo low-energy umbrella distortions leading to tetrahedral sulfur coordination. Though pyrosulfate is more stable at low temperature, at high temperature it is driven by entropy to lose SO_3, yielding sodium sulfate.

Acknowledgment. We are warmly appreciative to Drs. William L. Fielder, Fred J. Kohl, and Carl A. Stearns of the NASA Lewis Research Center for advice concerning this work, which has been supported by NASA Grant NAG3-341.

Registry No. $Na_2S_2O_7$, 13870-29-6; NaCl, 7647-14-5; SO_2, 7446-09-5; O_2, 7782-44-7; SO_3, 7446-11-9.

(13) L. P. Kostin, L. L. Pluzhnikov, and A. N. Ketov, *Russ. J. Phys. chem.*, **49**, 2235 (1975).

Theoretical Study of the Triple Metal Bond in d^3-d^3 Binuclear Complexes of Chromium, Molybdenum, and Tungsten by the Hartree-Fock-Slater Transition State Method

Tom Ziegler

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4. *Received April 25, 1983*

Abstract: Hartree-Fock-Slater calculations are reported for the two metal fragments MoL_3 and CrL_3 with L = H, CH_3, Cl, NH_2, and OH. The ML_3 systems all have a trigonal planar geometry with the metal-to-ligand bond strength in the order OH > Cl > NH_2 > CH_3 > H. The bonding energies of MoL_3 are somewhat larger than the corresponding energies of CrL_3. Hartree-Fock-Slater calculations are also reported for the two binuclear systems Mo_2L_6 and Cr_2L_6 with L = H, CH_3, Cl, NH_2, and OH. The staggered conformation is the preferred geometry for all the systems. The optimized metal-metal bond distances are calculated to be in the range 2.22 to 2.25 Å for the Mo systems and in the range 1.91 to 1.95 Å for the Cr systems. The strength of the metal-metal bonds follows the order Mo-Mo (468-414 kJ mol^{-1}) > Cr-C (301-217 kJ mol^{-1}). A study of W_2H_6 showed that the inclusion of relativistic effects increased the metal-metal bond energy from 422 to 535 kJ mol^{-1}.

1. Introduction

There has recently been considerable interest in the electronic structure of binuclear d^3-d^3 complexes following the synthesis and structural characterization of several M_2L_6 systems[1] with M = Mo and W.

A qualitative outline of the bonding in M_2L_6 was first given by Albright and Hoffmann.[2] The authors suggested that the observed staggered conformation of M_2L_6 is due to steric repulsions between ligands on different metal centers. It was proposed that the eclipsed conformation, favored by electronic factors according to ref 2, would be adopted by M_2L_6 for small-size ligands.

It has recently been possible to carry out ab initio calculations on binuclear metal compounds. Kok and Hall[3] have, in connection with a previous work, published results from ab initio calculations on Mo_2H_6 and $Mo_2(NH_2)_6$. They calculated the Mo-Mo bond strength D(Mo≡Mo) in Mo_2H_6 to be 118 kJ mol^{-1} and suggested, based on an error analysis, that a more extensive treatment (larger size configuration interaction) would give D(Mo≡Mo) as 248 kJ mol^{-1}. Tentative calculations on $Mo_2(NH_2)_6$ indicated that the replacement of L = H with L = NH_2 might increase D(Mo≡Mo) further by 117 kJ mol^{-1}. The best experimental determination[4] of D(Mo≡Mo), due to Adedeji et al.,[4] gives D(Mo≡Mo) as 398 kJ mol^{-1}. However, the experimental determination of D(Mo≡Mo) is somewhat hampered by uncertainties in the energy assigned to the Mo-L bonds.

Transition metal complexes have been studied extensively by the HFS method first suggested by Slater.[5] One of the most popular implementations of the HFS scheme is the Xα-SW method due to Johnson.[6]

Bursten, Cotton et al.[7] have recently published Xα-SW calculations on $Mo_2(NH_2)_6$, $Mo(N(CH_3)_2)_6$, $Mo_2(OH)_6$, and $Mo_2(CH_3)_6$. They provide a sophisticated analysis of the valence orbitals along with a correlation of calculated and experimental ionization potentials. Bursten et al.[7] dispute that the preferred geometry of M_2L_6 for small ligands should be eclipsed. They suggest that electronic factors would prefer a geometry for M_2L_6 for the two ML_3 fragments in a planar trigonal conformation and a free rotation around the metal-metal bond.

The Xα-SW scheme cannot calculate the total electronic energy accurately owing to an approximate representation of the molecular electronic potential. It is for this reason not possible to optimize molecular geometries or calculate bonding energies with the Xα-SW method.

We have used another implementation of the HFS method, due to Baerends et al.,[8] in which the molecular electronic potential

(1) (a) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. (b) Chrisholm, M. H.; Cotton, F. A. *Ibid.* **1978**, *11*, 356.
(2) Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736.
(3) Kok, R. A.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 728.
(4) Adedeji, F. A.; Cavell, K. J.; Cavell, S.; Connor, J. A.; Pilcher, G.; Skinner, H. A.; Safarani-Moattar, M. T. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 603.
(5) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1.
(6) Johnson, K. H. *J. Chem. Phys.* **1966**, *45*, 3085.
(7) Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *J. Am. Chem. Soc.* **1980**, *102*, 4579.
(8) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1976**, *2*, 41. (b) Baerends, E. J.; Ros, P. *Int. J. Quantum Chem.* **1978**, *S12*, 169.

0002-7863/83/1505-7543$01.50/0