THE JOURNAL OF PHYSICAL CHEMISTRY A

Addition/Correction

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Correction to "Activation Barriers in the Growth of Molecular Clusters Derived From Sulfuric Acid and Ammonia"

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Supporting Information

The authors would like to correct numerical errors in the paper and clarify points that were insufficiently described.

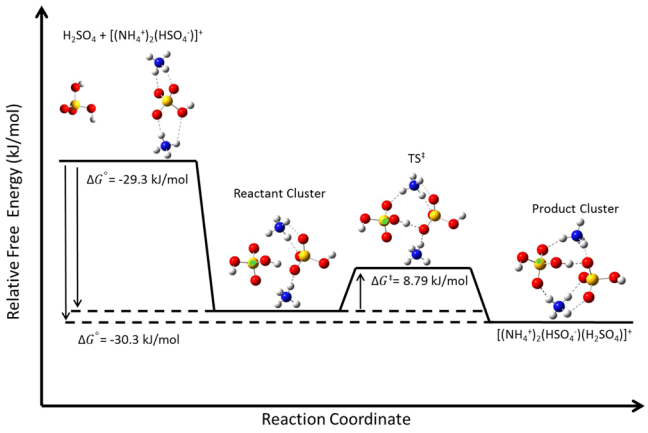

Figure 1 (Revised). Reaction path for first sulfuric acid addition to the $[(NH_4)_2(HSO_4)]^+$ cluster.

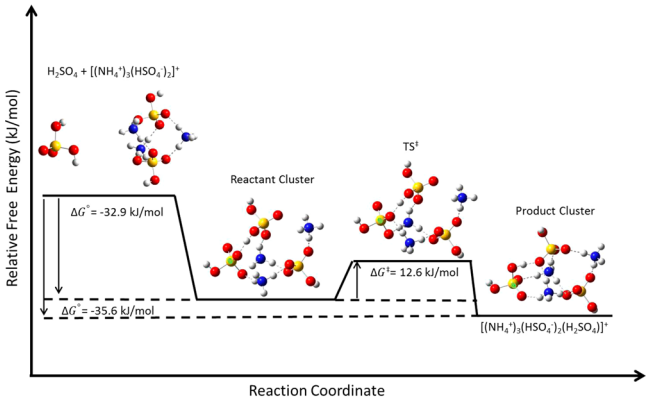

Figure 2 (Revised). Reaction path for the second sulfuric acid addition to the $[(NH_4)_3(HSO_4)_2]^+$ cluster.

These corrections and clarifications are embodied in the five revised figures shown herein plus the revised Supporting Information.

An effort to simplify the figures in the paper resulted in the mislabeling of several structures and energy increments. There are also numerical and transcription errors in Table 1 and the original SI file, which are corrected in the new SI file. Errors in the figures are corrected in the more complete figures below, which follow each small molecule addition to a growing cluster from separated reactants through a loosely bound preassociation complex (referred to as a "reactant cluster" in the paper) over a transition state to the resulting larger product cluster. The original figures begin with the preassociation complex and provide correct barriers to the formation of the final product cluster but fail to give correct binding energies and correct structures of the preassociation complexes.

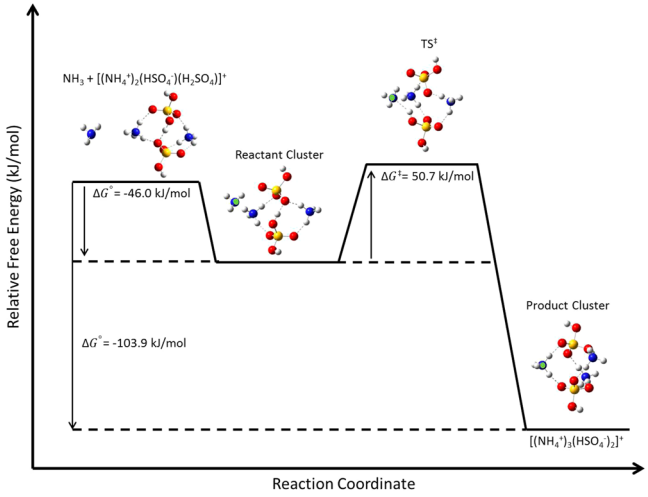

Figure 3 (Revised). Reaction path for the first ammonia addition to the $[(NH_4)_2(HSO_4)(H_2SO4)]^+$ cluster.

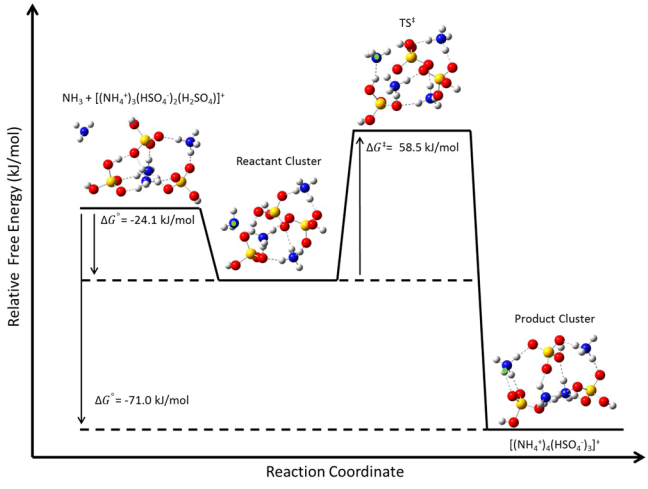

Figure 4 (Revised). Reaction path for the second ammonia addition to the $[(NH_4)_3(HSO_4)_2(H_2SO4)]^+$ cluster.

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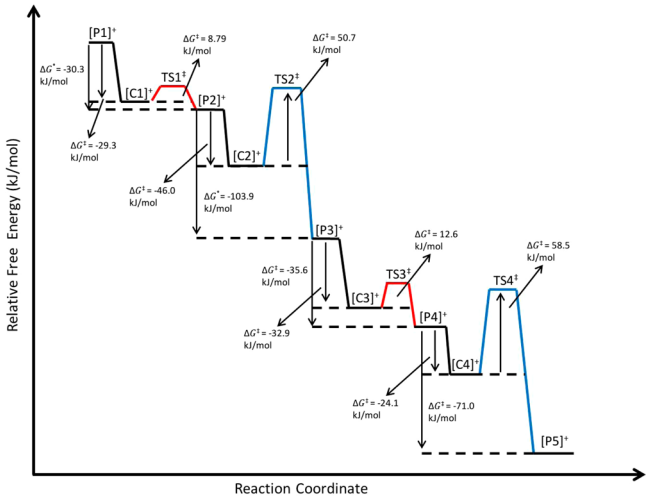

Figure 5 (Revised). Complete reaction path with all energies for the ammonium bisulfate cluster growth pathway.

The corrections do not change the conclusions in any fundamental way. Using the preassociation binding energies in place of the generic estimated electrostatic energies gives values of γ in somewhat better agreement with experiment. For an association reaction proceeding through a preassociation complex at atmospheric pressure, the effective free energy of activation is the sum of the free energy change of the preassociation complex and the activation free energy of proceeding from the preassociation complex to the transition state. The values of γ obtained are 1, 0.1, 1, and 10^{-6} for reactions 1, 2, 3, and 4, consistent with the general conclusion that sulfuric acid addition is efficient while ammonia addition faces an energetic barrier and also consistent with the same general conclusion suggested by the experimental studies discussed in the original paper.

While a number of sets of the required initial guesses of reactants, transition states, and products were investigated, the results reported represent the lowest-energy IRC-connected pathways found for each reaction. The possibility of lower energy pathways cannot be eliminated with complete certainty due to the shallow potential energy surfaces for the formation of hydrogen-bound molecular complexes.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENTS

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