

ADDITIONS AND CORRECTIONS

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Glen P. Jackson, Fred L. King, Douglas E. Goeringer, and Douglas C. Duckworth*: Gas-Phase Reactions of U^+ and U^{2+} with O_2 and H_2O in a Quadrupole Ion Trap

Pages 7788–7794. It has been brought to our attention that the upper limit determined¹ for the enthalpy of formation for $UO^{2+}(g)$ was calculated using the invalid assumption that exothermic charge-transfer reactions involving dications of uranium-containing species would not show a kinetic barrier, as is commonly applied to bracketing experiments with singly-charged ions. Using this invalid assumption, we calculated an upper limit for $\Delta H_f(UO^{2+}(g))$ as 1747 kJ mol^{-1} , which is considerably lower than the previous upper limit of 2047 kJ mol^{-1} established by Cornehl and co-workers.² We have since learned of a curve-crossing model that describes a kinetic barrier to exothermic charge transfer reactions involving a doubly charged reagent ion and two singly charged products.^{3–9}

The curve crossing phenomenon explains why oftentimes upward of 1.5 eV of exothermicity is required to drive a charge transfer reaction between a doubly charged cation and neutral.⁵ Mildly exothermic charge transfer reactions between dications and neutrals ($-150 \text{ kJ mol}^{-1} < \Delta H_{\text{reaction}} < 0 \text{ kJ mol}^{-1}$) are often not observed.^{5,8} Considering this phenomenon, our upper limit for $\Delta H_f(UO^{2+}(g))$ could be underestimated by up to $\sim 250 \text{ kJ mol}^{-1}$,⁵ which does not improve significantly on the previous limit of 2047 kJ mol^{-1} determined by Cornehl et al.²

In addition, the same curve-crossing phenomenon suggests that the lower limit that we derived for $\Delta H_f(UOH^{2+}(g))$ is also underestimated by some unknown degree (possibly $150\text{--}250 \text{ kJ mol}^{-1}$)⁵ and actually improves the bracketing value obtained for this species. However, due to the uncertainty of the excess exothermicity required to drive these reactions, we refrain from estimating actual limits. These results do not affect the other thermodynamic and kinetic data determined in the original manuscript.

References and Notes

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