

2005, Volume 109B

Jayakumar Narayanasamy and James D. Kubicki*: Mechanism of Hydroxyl Radical Generation from a Silica Surface: Molecular Orbital Calculations

In our recent paper,¹ the rate constants calculated were not for strictly gas-phase reactions, but for surface reactions, so we should not have used the translational and rotational partition functions to calculate the rate constants of the reactions. Surface reaction rate constants should be calculated from only from the vibrational partition functions.²

The rate constants as a function of temperature, $k(T)$, were recalculated with the following equations:

$$k(T) = (k_B T/h)(q_{TS}^{\text{vib}}/q_{\text{React}}^{\text{vib}}) \exp(-\Delta E_a^0/RT) \quad (1)$$

$$k(T) = (k_B T/h)(q_{TS}^{\text{vib}}/q_{\text{Prod}}^{\text{vib}}) \exp(-\Delta E_a^0/RT) \quad (2)$$

for the forward and reverse reactions, respectively. ΔE_a^0 is the activation energy barrier with zero-point energy correction. q_{TS}^{vib} , $q_{\text{React}}^{\text{vib}}$, and $q_{\text{Prod}}^{\text{vib}}$ are the vibrational partition functions for the transition state, reactants, and products of the reaction, respectively (see ref 3 for more background).

In addition to listing inaccurate rate constants in Tables 6 and 7 of Narayanasamy and Kubicki,¹ the Arrhenius parameters derived through VKLab⁴ by fitting $\ln k(T)$ versus $(1/T)$ did not make sense. This is because, in our earlier calculations, the transition states for reactions 1 and 4¹ were not correct. The configurations used as transition state structures resulted in two (rather than only one) imaginary frequency. New results are given in the Supporting Information.

The main implication of these revisions is that the following statement we made in the original paper was wrong.

When H₂O reacting on a surface with radical sites is compared, reaction with the ≡SiO• site to produce OH• would be more rapid than that with the ≡Si• site to produce H•, which is opposite to the interpretation found in Saruwatari et al.⁵ to explain H₂ gas production by fractured silica interacting with water.

The corrected results presented here are consistent with Saruwatari et al.⁵ in that the H• should be produced faster initially, allowing production of H₂ gas as two H• species react with one another.

Supporting Information Available: Tables showing optimized key geometry parameters, recalculated potential energies, ZPEs, potential energies after ZPE corrections, Gibbs free energies, calculated forward and backward rate constants, and pre-exponential factors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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10.1021/jp062377i

Published on Web 07/22/2006