On the competing hydrations of sulfur dioxide and sulfur trioxide in our atmosphere

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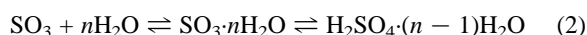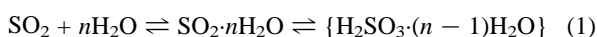
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It is demonstrated that in our atmosphere sulfur trioxide (SO_3) is hydrated rather than the much more abundant sulfur dioxide (SO_2), *i.e.* atmospheric oxidation precedes hydration.

In our atmosphere sulfur dioxide is converted to sulfuric acid, a major component of acid rain, and sulfates, which increase Earth's reflectance by forming nuclei for cloud condensation. The pathway of this conversion is constituted of both an oxidative and hydration step. Whether SO_2 is first oxidized, as proposed by Stockwell and Calvert,[1] or first hydrated is still not fully clear. The direct oxidation of SO_2 by the hydroxyl radical proceeds either without[2] or with a very small energy barrier.[3] Also the activation barrier for oxidation of 'hydrated SO_2' ($HOSO_2^-$) by H_2O_2[4,5] or O_2[6] is rather low. Vincent, Hillier and Palmer conjectured that in fact SO_2 and not the hydrogensulfite anion ($HOSO_2^-$) is oxidized.[5] These low barriers indicate that both oxidations are fast. In order to investigate which of the two possible hydrations is fast or slow, we have performed direct dynamics calculations on reactions (1) and (2)

$$SO_2 + nH_2O \rightleftharpoons SO_2 \cdot nH_2O \rightleftharpoons \{H_2SO_3 \cdot (n-1)H_2O\} \quad (1)$$

$$SO_3 + nH_2O \rightleftharpoons SO_3 \cdot nH_2O \rightleftharpoons H_2SO_4 \cdot (n-1)H_2O \quad (2)$$

where the size of the involved water-cluster varies from $n = 1$ to 3. For reaction (2) both laboratory studies[7,8] and direct dynamics studies by us[9] on the atmospheric reaction rate constants showed that owing to hydration to sulfuric acid, the lifetime of SO_3 is comparable to that of SO_2 which undergoes oxidation by hydroxyl radicals. The good agreement in the obtained rates demonstrates the reliability of the theoretical methods, namely variational transition state theory corrected for microcanonical optimized multidimensional tunneling on the basis of a hybrid density functional theory potential energy surface [B3LYP/6-31+G(d)].[10,11] Because of the thermodynamic instability of 'sulfurous acid' (H_2SO_3) this species has never been isolated, and accordingly no experimental studies have been performed on reaction (1). This instability has been noted in the literature[12] and is here confirmed to amount to 6.8 kcal mol^{-1} in electronic energy at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory. Application of the theoretical approach to the unimolecular isomerization in reaction (1) leads to the reaction rates shown in Fig. 1. It becomes clear that the hydration of SO_3 is much faster than the hydration of SO_2 if more than one water molecule is allowed to participate for all temperatures prevailing in our atmosphere. Only in the case of very low water vapor pressures, under which conditions no complexes of $>1{:}1$ stoichiometry form, and at temperatures below 150 K the hydration of SO_2 is faster than the one of SO_3. However, 'faster' here in fact means 'less slow' as both conversions are unmeasurably slow under such conditions. In contrast to the facile and fast reactions in aqueous solution ($k = 3.4 \times 10^6$ s^{-1})[13] and the gas–liquid interface[14] the pure gas-phase process involving SO_2–water clusters[15] is very slow. As

a consequence, the reaction path not involving hydration of SO_2, namely oxidation of SO_2 with subsequent hydration of SO_3, will be favored under atmospheric conditions. This arises mainly from the fact that the barrier for the SO_2 hydration decreases from 33 kcal mol^{-1} ($n = 1$) to 20 kcal mol^{-1} ($n = 2$) and 13 kcal mol^{-1} ($n = 3$), whereas the barrier for hydration of SO_3 decreases from 28 kcal mol^{-1} ($n = 1$) to 4 kcal mol^{-1} ($n = 3$, rotary)[9] according to the B3LYP/6-31+G(d) level of theory. At the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory taking electron correlation more accurately into account, the barriers are different by at most 10%. In the literature at the G2[16] and QCISD(t) levels[12] the barriers are also found to be similar.

Additionally, the preassociation reaction forming the hydrogen bonded complex is more favorable for SO_3 than for SO_2, as indicated by a gain in electronic energy of 19.8 kcal mol^{-1} compared to 14.7 kcal mol^{-1} [CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ values for $n = 2$]. Therefore, the difference in the overall rate constant is increased by four orders of magnitude at 250 K in addition to the difference seen in Fig. 1. For a first order rate law for SO_2 or SO_3 this implies that the SO_2 pressure has to be 10 orders of magnitude higher than the SO_3 pressure at 250 K and as much as 20 orders of magnitude higher at 150 K for SO_2 hydration to become competitive. However, at an altitude of 30 km the steady state concentration of SO_3 of *ca.* 10^5 molecules cm^{-3} compared with that of SO_2 of *ca.* 10^{10} molecules cm^{-3} is only lower by 5 order of magnitude.[8] It is, therefore, safe to assume that the dominant mechanism converting S(IV) to S(VI) species if *first* the oxidation of SO_2 by OH$^\bullet$ and *second* the isomerization of a SO_3–H_2O cluster of a
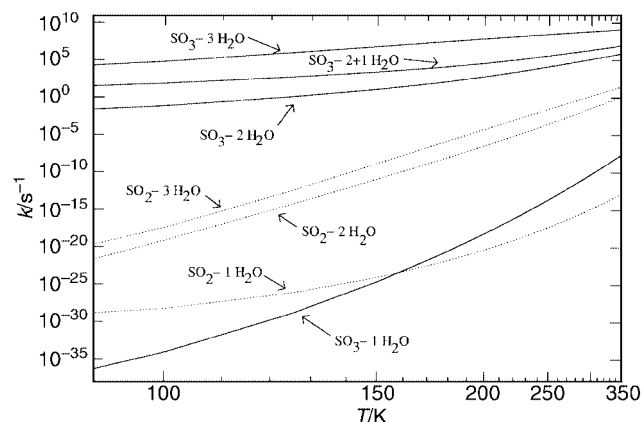

Fig. 1 Arrhenius plot of the hydration reactions of sulfur trioxide (——) and sulfur dioxide (······) in the presence of up to three water molecules in the unimolecular complex. The meaning of n is explained in Fig. 2 for SO_2 and in our previous work for SO_3.[9]
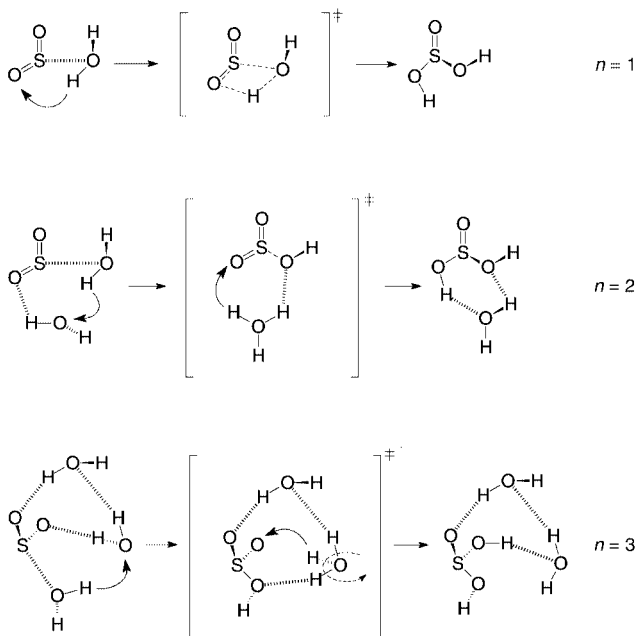
Fig. 2 Qualitative representation of the stationary points of the different unimolecular isomerization steps of the hydration of SO_2. Water addition concerted with a single proton transfer in the presence of a single water molecule ($n = 1$), hydration concerted with sequential water-mediated double proton transfer ($n = 2$), and hydration concerted with the sequence proton transfer–rotation of H_3O^+-proton transfer in the presence of a third stabilizing water molecule ($n = 3$).

stoichiometry of 1:2 or higher, since slow hydration of SO_2 is circumvented.

Notes and references

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