Sulfur dioxide oxidation induced mechanistic branching and particle formation during the ozonolysis of β-pinene and 2-butene†

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Recent studies have suggested that the reaction of stabilised Criegee Intermediates (CIs) with sulfur dioxide (SO2), leading to the formation of a carbonyl compound and sulfur trioxide, is a relevant atmospheric source of sulfuric acid. Here, the significance of this pathway has been examined by studying the formation of gas phase products and aerosol during the ozonolysis of β-pinene and 2-butene in the presence of SO2 in the pressure range of 10 to 1000 mbar. For β-pinene at atmospheric pressure, the addition of SO2 suppresses the formation of the secondary ozonide and leads to highly increased nopinone yields. A complete consumption of SO2 is observed at initial SO2 concentrations below the yield of stabilised CIs. In experiments using 2-butene a significant consumption of SO2 and additional formation of acetaldehyde are observed at 1 bar. A consistent kinetic simulation of the experimental findings is possible when a fast CI + SO2 reaction rate in the range of recent direct measurements [Welz et al., Science, 2012, 335, 204] is used. For 2-butene the addition of SO2 drastically increases the observed aerosol yields at higher pressures. Below 60 mbar the SO2 oxidation induced particle formation becomes inefficient pointing to the critical role of collisional stabilisation for sulfuric acid controlled nucleation at low pressures.

The atmospheric abundance of sulfuric acid (H2SO4) is closely related to observations of new particle formation.1 The dominant H2SO4 forming pathway of atmospheric relevance is assumed to start with the oxidation of sulfur dioxide (SO2) to sulfur trioxide (SO3) by the OH radical.2 Low-volatility organic compounds are believed to contribute to the subsequent growth of the clusters to nanoparticles.3 Such highly oxidized species are formed in the atmospheric degradation of many hydrocarbons from biogenic and anthropogenic sources by OH, NO3 and ozone.4

The importance of cross reactions between organic chemistry and sulfur chemistry for aerosol formation during alkene ozonolysis is known for a long time.4,8 Hatakeyama et al. analysed the particle formation during the ozonolysis of 2-butene and other alkenes in the presence of SO2.6 An intriguing result of this early work was the reduction of sulfuric acid yields in aerosol samples from trans-2-butene with decreasing pressure, reaching zero at the lowest pressures. The authors concluded that SO2 is oxidized by stabilised Criegee Intermediates (CIs). 20 years later Berndt et al. concluded for the ozonolysis of 2-butene (as well as β-pinene and tetramethylethylene) in the presence of SO2 that the oxidation of SO2 by OH is the dominant pathway for H2SO4 formation but at the same time reported significant contributions from CI + SO2. We note that Berndt et al. used much lower reactant concentrations being close to atmospheric conditions. For cyclohexene + O3 we found in previous work a relation of generated particle number densities and SO2 concentrations, which were at low H2SO4/SO2 concentrations consistent with SO2 + OH being the only source of sulfuric acid.9

In a recent paper the first direct kinetic measurements of the reaction of the CI–CI (CH3CHO) with SO2 were reported employing single photon, near threshold ionization for specific CI detection.10 The measured rate coefficient was significantly faster than previously believed (3.9 × 10−11 cm³ s⁻¹ compared to 0.04 to 8 × 10−15 cm³ s⁻¹, see discussion in ref. 10), providing experimental evidence for theoretical work of Kurtén et al. on the oxidation of SO2 to SO3 by gas-phase organic oxidants.11 These results suggested that CI + SO2 may contribute significantly to atmospheric H2SO4 production. This interpretation is bolstered by a current combined field and laboratory study.12 However, due to the experimental approach the direct kinetic measurements were performed at 4 Torr and have not been extended to substituted CIs at atmospheric pressure.13 The aim of the present study is to bridge this gap by studying the CI + SO2 reaction in the context of pressure dependent mechanistic branching and aerosol formation during alkene ozonolysis. The alkenes under study are β-pinene and 2-butene (mixture of cis and trans), which produce predominantly14 or solely substituted CIs in the reactions with ozone.

Direct kinetic measurements are highly desirable but unfortunately limited by the availability of suitable precursors for the photodissociation induced specific preparation of larger CIs. Therefore we make use of the growing network of interdependencies for ozonolysis reactions.14–16 In the case of β-pinene, a recent extensive theoretical study provided crucial kinetic information which is needed for robust modelling of the first reaction steps.14 For the ozonolysis of 2-butene the results of absolute rate coefficient determinations of reactions involving the C2–CI (CH3CHO) are available.17

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All ozonolysis experiments were performed in our static variable pressure reaction chamber with a volume of 64 L and two premixing chambers of 40 L volume. One of them is used as an ozone reservoir and is equipped with UV optics for a continuous measurement of O₃ concentrations. Concentrations of reactants and the product yields were determined using infra-red spectroscopy (Bruker IFS 66, 12 m path length in the cell). SO₂ concentrations were determined by means of IR spectroscopy and volumetry as described in detail in a recent paper.⁹ A particle classifier (TSI SMPS 3936 with NDMA (3085) and LDMA (3081) as well as a 3022 CPC (condensation particle counter)) was used for particle measurements (operation parameters: 2 litres per minute (lpm) sheath flow and 0.2 lpm sample flow). The pressure variation was achieved by expanding the reactants from the premixing chambers into the evacuated reaction cell within 3 s. For starting pressures between 25 and 1000 mbar this procedure results in final pressures between 10 and 450 mbar. For experiments at higher pressures additional synthetic air is filled in the reaction cell directly after the expansion (approx. 15 s filling time). The fast reactant mixing allows the use of relatively high initial concentrations which effectively suppress the heterogeneous loss of reactants and products to the wall. Further details on the apparatus and the applied procedures are given in recent papers.⁹,¹⁶ All chemicals used were of commercial grade (see ESI).

First, we discuss the results for the ozonolysis of β-pinene. This terpene is of atmospheric relevance and many experimental and theoretical studies have been published on this reaction (ref. 14, 16, 18–22 and references therein) with the focus on both stable gas phase product formation and the production of SOA. The extensive theoretical study of Nguyen et al. revealed that two distinct, non-interconvertible conformers of C⁹–CI (–COO function either points to or away from internal ring, see ref. 14) are formed. Only 5% CH₂OO yield was predicted. These properties of β-pinene ozonolysis indicate that this is a suitable system for studying mechanistic features related to the reactions of larger substituted, biogenic CIs with SO₂. The key observations for such experiments are illustrated in the upper panels of Fig. 1. Addition of 3 ppm SO₂ to an initial mixture of 9 ppm O₃ and 30 ppm β-pinene has two significant effects on the IR final product spectrum: the additional formation of a carbonyl compound and the reduced formation of a product with a characteristic double peak near 1100 cm⁻¹ (features A and B in the IR difference spectrum, upper panel of Fig. 1). Feature B was previously assigned to a secondary ozonide (SOZ).¹⁶,¹⁹ The carbonyl compound is most likely nopinone, which is deduced from the fit of the C—O stretch band and other characteristic nopinone features when compared to a pure product spectrum (see Fig. S1 in the ESI†). In addition, we observe a complete consumption of SO₂ at 1 bar (see the lower trace in the left middle panel of Fig. 1). At 10 ppm initial concentration unreacted SO₂ is observed in the end product spectrum. At this initial SO₂ concentration the characteristic SOZ features are completely suppressed (see the right middle panel of Fig. 1). All these findings can be explained by the direct oxidation of SO₂ to SO₃ via the fast reaction with a stabilised CI.⁷,¹⁰,¹¹ If SO₂ is predominantly consumed via CI + SO₂ the picture will change at low pressure where a much lower fraction of CIs is stabilised enough to take part in bimolecular reactions.¹⁴ The upper trace

![Fig. 1](image-url)
reports (see Hasson et al.24). An in-depth analysis of this interesting effect should include the isomer distinction of 2-butene, a rigorous calibration of the additional carbonyl compound formation as a function of pressure and – where possible – relative to adduct formation.7 This is beyond the scope of this communication and will be addressed in a subsequent full length paper. Several test experiments were performed for all alkenes using cyclohexane as an OH scavenger. No measurable effect on the SO2 consumption was observed.

In the next section the experimental results are compared to predicted product yields derived by kinetic modelling of the ozonolysis reaction. To this end the mechanism applied in the preceding work9 has been adopted to the alkenes under study using kinetic data provided by Nguyen et al.14 for β-pinene and Fenske et al. for 2-butene.17 We have now included the Cl + SO2 reaction which was not considered for cyclohexene + O3 due to the absence of stabilised CIs.15 Further details on the kinetic modeling are given in the ESI†.

We simulated the ozonolysis of β-pinene for the conditions given in the caption of Fig. 1 with an initial amount of 3 ppm SO2 using different rate coefficients for the CI + SO2 reaction. A complete consumption of SO2 as observed in the experiment is only predicted when a value larger than 1 × 10^-11 cm^3 s^-1 is applied (see Fig. 2). Use of a rate coefficient of 1 × 10^-11 cm^3 s^-1 would according to the simulation result in a final SO2 concentration of 0.3 ppm, which is not observed in the experiment (see the left middle panel of Fig. 1). Similar results were obtained for 2-butene + O3 and the partial consumption of SO2 (see Fig. S3 in the ESI†). Also for this alkene the best agreement between experimental findings and model predictions is found when a high value for k(CI + SO2), larger than 1 × 10^-11 cm^3 s^-1, is used. These findings suggest that the direct measurements of Welz et al. for k(CI + SO2) at 4 Torr give a suitable estimate for larger CIs at higher pressure. However, we note here that the modelling results depend to some degree on the yields of stabilised CIs. If the added amount of SO2 exceeds the applied fraction of stabilised CIs the simulation predicts that SO2 is not completely consumed for simple stoichiometric reasons. This implies an intrinsic uncertainty of model predictions regarding the final SO2 concentrations. We further note that the conditions of our experiment (relatively high initial reactant concentrations) favor bimolecular chemistry over the consumption of CIs by unimolecular reactions. Assuming unimolecular rates in the range of 1 to 100 s^-1 would only slightly change the predicted consumption of SO2 in case of β-pinene, for 2-butene the influence would be larger. However, Nguyen et al.14 found a consistency of their predicted and experimentally determined17 isomerisation rates of thermalised CIs for the two alkenes under study. In the light of these considerations we hesitate to use a simple best fit of k(CI + SO2) to match the point where the final SO2 concentration is below the detection limit to pinpoint the rate coefficient. Nonetheless, the combined results of experiments and kinetic modelling suggest that k(CI + SO2) is likely above 1 × 10^-11 cm^3 s^-1 and clearly above 3 × 10^-12 cm^3 s^-1 for both alkenes under study. Independent evidence for this lower limit in the case of β-pinene comes from the observed suppression of SO2 formation (see Fig. 1 and Fig. S4 in the ESI†) where the relative rate of CI + carbonyl and CI + SO2 is probed. The effective suppression shows that the latter reaction is much faster. However, we have to state that the evidence from kinetic modelling is limited in case fast, yet unexplored SO2 consuming reactions exist. Furthermore, alkene specific rates have to be considered (see ref. 12 for results on α-pinene and limonene). A critical point for both kinetic modelling and experimental studies is the unimolecular rate coefficients of isomerisation reactions of stabilised CIs. Assuming in the kinetic simulation significantly lower unimolecular reaction rates than reported by Fenske et al.17 would in case of 2-butene allow a consistency with a lower range of values for k(CI + SO2). We note that measurements at low initial reactant concentrations, which employ the detection of the product H2SO4, are more closely linked to unimolecular CI chemistry. Here, the rate coefficient k(CI + SO2) is measured relative to the CI loss rate. Another important point is that measuring H2SO4 formation instead of CI or SO2 consumption would lead to lower k(CI + SO2) values when CI-SO2 adducts are stabilised to a significant degree (see also discussions in ref. 12, 14 and 26).

In the following the key results on aerosol yields as a function of SO2 addition will be discussed. All experiments were performed at 450 mbar to achieve a high reproducibility by fast reactant mixing.9 For 2-butene the observed SO2 consumption and acetaldehyde formation suggest an effective production of H2SO4. The kinetic model predicts H2SO4 formation via CI + SO2 to be at least two orders of magnitude faster than via OH + SO2. This should manifest itself in a large influence of SO2 addition on the observed aerosol formation. In the left panel of Fig. 3 particle numbers from

![Fig. 2](image_url)

Fig. 2 Simulated mole fraction profiles of SO2 for an initial mixture of 30 ppm β-pinene and 9 ppm ozone at 298 K and 1 bar using different rate coefficients for CI + SO2.

![Fig. 3](image_url)

Fig. 3 Left panel: particle numbers as a function of added SO2 concentrations for the ozonolysis of 2-butene (1 Pa 2-butene, 0.1 Pa O3) at 450 mbar. Right panel: pressure dependence of particle numbers upon addition of 0.01 Pa SO2 and 0.1 Pa O3. Error bars (95% confidence interval) were derived exemplarily from experiments under fixed conditions.
2-butene ozonolysis (1 ppm ozone, 10 ppm 2-butene) as a function of the added amount of SO₂ are shown. In the absence of SO₂ no particle formation is observed, above 0.0004 Pa (4 ppb at 1 bar) SO₂ aerosol formation starts and is highly intensified when the fraction of SO₂ in the mixture is further increased. This finding suggests that SO₂ oxidation by CIs provides an efficient and kinetically controllable gas phase source of sulfuric acid, which can be used to study H₂SO₄-induced nucleation dynamics in laboratory experiments. When reducing the pressure a slight decrease in particle numbers between 450 and 60 mbar is found. This effect can be related to the pressure dependence of stabilised CI yields (see results for the related alkenes, ethylene and tetramethylethylene[15,25]). Below 60 mbar, however, the particle formation is significantly reduced which is a similar finding to our previous work on SO₂ oxidation induced aerosol formation during cyclohexene ozonolysis, pointing to the critical role of collisional stabilisation for H₂SO₄ induced particle formation.[9] The effect on observed particle numbers upon adding SO₂ during β-pinene ozonolysis is much weaker because particles are effectively formed in the absence of SO₂ (see Fig. S5 in the ESI).[16]

Different from α-pinene ozonolysis[8] we find additional aerosol mass build up below 100 mbar for β-pinene which again can be explained by the much higher abundance of stabilised CIs in the case of β-pinene at low pressure.[14,15]

In summary, we have characterized several effects of SO₂ addition on final gas phase product and aerosol formation during the ozonolysis of β-pinene and 2-butene. The experimental findings, namely the efficient SO₂ consumption, additional carbonyl and suppressed SOZ formation in combination with the kinetic modelling result in a consistent picture when a fast reaction of stabilised CIs with SO₂ at ambient pressure is assumed. Thus the direct kinetic results of Welz et al. on the CH₂OO + SO₂ reaction at low pressure[10] seemingly provide a reliable estimate for larger, substituted CIs at tropospheric pressure. At the same time we have to be aware that uncertainties concerning the unimolecular reaction rates of stabilised CIs and an incomplete understanding of H₂SO₄ formation pathways may imply systematic errors which cause discrepancies between different experimental approaches.[10,12,14,17,26] Therefore additional direct measurements of CI + SO₂ reactions rates are desirable. The observed effects on particle formation under SO₂ addition give additional experimental evidence for both the important role of the CI + SO₂ reaction in atmospheric aerosol formation[12] and the inefficiency of sulfuric acid based nucleation at low pressures.[9]

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