Atmospheric Chemistry **Hot Paper**

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Infrared Detection of Criegee Intermediates Formed during the Ozonolysis of β-Pinene and Their Reactivity towards Sulfur Dioxide**

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Abstract: *Recently, direct kinetic experiments have shown that the oxidation of sulfur dioxide to sulfur trioxide by reaction with stabilized Criegee intermediates (CIs) is an important source of sulfuric acid in the atmosphere. So far, only small CIs, generated in photolysis experiments, have been directly detected. Herein, it is shown that large, stabilized CIs can be detected in the gas phase by FTIR spectroscopy during the ozonolysis of β-pinene. Their transient absorption bands between 930 and 830* cm^{-1} *appear only in the initial phase of the ozonolysis reaction when the scavenging of stabilized CIs by the reaction products is slow. The large CIs react with sulfur dioxide to give sulfur trioxide and nopinone with a yield exceeding 80%. Reactant consumption and product formation in time-resolved β-pinene ozonolysis experiments in the presence of sulfur dioxide have been kinetically modeled. The results suggest a fast reaction of sulfur dioxide with CIs arising from β-pinene ozonolysis.*

The oxidation of terpenes in the troposphere contributes to the formation of secondary organic aerosol (SOA), which is known to have a significant effect on the earth's climate.[1] However, there is substantial uncertainty about the molecular mechanisms in operation.[1] Field observations and experimental studies have shown that the frequency of new-particle-forming events is correlated to the abundance of sulfuric acid in the atmosphere.[2] A major source of tropospheric sulfuric acid is the reaction sequence that starts with the oxidation of sulfur dioxide by the hydroxyl radical.[2,3] Another pathway is the oxidation of sulfur dioxide to sulfur trioxide by the reaction with Criegee intermediates (CIs).[4,5] CIs are formed during the ozonolysis of alkenes by the decomposition of the primary ozonide (POZ) to give the CI and a carbonyl compound (or a corresponding moiety for endocyclic alkenes).[6] It was recently shown by direct kinetic measurements[7,8] that the small stabilized Criegee intermediates (sCIs) CH_2OO and CH_3CHOO (both conformers) react much faster with SO_2 than previously assumed.[9] These new experiments used a photolytic precursor (diiodoalkanes) of sCIs. Using the same photolytic approach, the smallest CI (CH_2OO) was recently detected by IR spectroscopy.[10] Recent indirect kinetic studies on the reaction $sCI + SO_2$ employing alkene ozonolysis as the sCI source either agree[11] or disagree[12] with the direct measurements.

Biogenic terpenes such as α-pinene and β-pinene are abundant volatile organic compounds, and their concentrations are monitored in field observations.[13] Therefore, it is crucial to determine reliable kinetic data for sCIs produced by the ozonolysis of these species. Very recently Boy et al. analyzed the effect of including new, larger rate coefficients for $sCI + SO_2$ reactions in atmospheric models.[13] The result was a drastic change of the current understanding of the production of sulfuric acid in the atmosphere: based on the kinetic analysis of data recorded at two field observation stations, 33–46% of the sulfuric acid formed at ground level was predicted to arise from oxidation of SO_2 by Criegee intermediates. However, for the reaction of sCIs from the ozonolysis of β-pinene a rate coefficient was applied that was still 50 times lower than the results from Refs. [7,11], reflecting the disagreement between the most recent studies.

This situation calls for new experimental approaches to obtain reliable information on the reaction kinetics of the $sCI + SO_2$ reaction for CIs from biogenic alkenes at ambient pressure. In the present work we show that sCIs can be detected directly during the ozonolysis reaction by taking advantage of characteristic chemical time scales as well as some mechanistic features of the ozonolysis[6] and IR absorption properties of CIs. Furthermore, we show that by refining our earlier approach,[11] in which we combined the IR detection of reactants and products with detailed kinetic modeling, we obtain kinetic constraints for the $sCI + SO_2$ reaction during β-pinene ozonolysis.

The experiments were performed under dry conditions (estimated residual water ca. 3 ppm, see Ref. [11]) in a static, variable-pressure reaction chamber with a volume of 64 L and two premixing chambers each with a volume of 40 L. One of them was filled with an ozone–helium mixture; UV optics were used for the continuous measurement of the ozone concentration. Ozone was generated by an ozonizer; synthetic air was used as a bath gas. Reactant and product concentrations were determined by using time-resolved FTIR spectroscopy (Bruker IFS 66, White optics, 12 m path length). Calibration spectra for the quantitative detection of stable species were derived by standard volumetric techniques as explained in earlier work (for details see, for example, Refs. [14,15]). The IR detection of the sCIs, the key result

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of this work, will be discussed in detail below. All chemicals used were of commercial grade (see the Supporting Information).

The reaction mixture consisting of ozone and β-pinene was prepared by expanding the reactants from the premixing chambers into the reaction cell within 1 s. This procedure promotes fast reactant mixing and provides a well-defined starting point for the ozonolysis reaction.[14,15] The experiments were performed at a pressure of (450 ± 10) mbar, resulting from 1 bar pressure in the premixing chambers. The mole fractions given below refer to 1 bar reference pressure. For the reaction kinetics, which are the focus of the present study, this deviation from atmospheric conditions is uncritical, as was shown in our previous work.[14,15] Additionally, a large amount of sCIs is formed at this pressure for the alkene under study, as will be shown below. An important aspect of our experimental approach is the application of relatively high reactant concentrations. For the initial stage of the reaction, this implies a dominance of bimolecular reactions over unimolecular steps and wall-loss processes.[14,15]

The initial reaction sequence for the β-pinene + O_3 reaction is well established (see, for example, Refs. [11,16,17]) and is described by Equations (1)–(7).

$$\beta\text{-pinene} + O_3 \rightarrow \text{POZ} \tag{1}$$

$$\text{POZ} \rightarrow \text{CI-1}\,(45\,\%) + \text{HCHO} \tag{2}$$

$$\text{POZ} \rightarrow \text{CI-2}\,(45\,\%) + \text{HCHO} \tag{3}$$

$$\text{POZ} \rightarrow CH_2OO\,(10\,\%) + \text{nopinone} \tag{4}$$

$$\text{CI-1/CI-2} + \text{M} \rightarrow \text{sCI-1/sCI-2} + \text{M}\ (30\,\%\ \text{at}\ 450\,\text{mbar}) \tag{5}$$

$$\text{CI-1/CI-2} \rightarrow \text{products}\ (70\,\%\ \text{at}\ 450\,\text{mbar}) \tag{6}$$

$$\text{sCI-1/sCI-2} + \text{HCHO} \rightarrow \text{SOZ} \tag{7}$$

The POZ decomposes promptly and cannot be detected in our experiment. About 40 % of the large CIs formed are collisionally stabilized at 1 bar; at 450 mbar this yield drops to about 30 % (see discussion below). A special feature of β-pinene ozonolysis is the predominant formation of large C_9-CIs (for the abbreviations CI-1 and CI-2, see Ref. [17], Figure 4, and the Supporting Information) over the small CI (CH_2OO). In our experiments without SO_2 the absorption features of the secondary ozonide (SOZ) centered at 1102 and 1060 cm^{-1} dominate the fingerprint region of the IR product spectrum (see the top panel of Figure 1 and Refs. [14,16]). In the presence of a sufficiently high concentration of SO_2, SOZ formation is completely suppressed. Instead, the C=O stretching region around 1750 cm^{-1} is dominated by the absorption band of nopinone (see the bottom panel of Figure 1). All these observations can be accounted for by assuming the fast reaction of SO_2 with large sCIs [Eq. (8)] on the basis of kinetic modeling of the end products ($k \approx 4 \times 10^{-11}\ cm^3 s^{-1}$).[11]

$$\text{sCI-1/sCI-2} + SO_2 \rightarrow SO_3 + \text{nopinone} \tag{8}$$

However, this evidence is indirect and coupled to the assumptions made in the kinetic modeling. These assumptions would be significantly corroborated if simulations included simultaneously measured concentration–time profiles of species that are chemically coupled to each other by reactions (1)–(8). This is possible because the reactants β-pinene and ozone as well as SO_2 and nopinone can be detected individually by their IR absorptions.[11] In Figure 2 reactant and SO_2 consumption together with nopinone formation are shown as a function of time for several initial concentrations. The IR absorption of the detected species was measured in time windows of 12–18 s, and concentrations based on the averaged absorbance are plotted for the middle of each time window. The initial reaction rate differs by a factor of 12 for the highest and lowest reactant concentrations. The experiments were kinetically modeled using the slightly modified mechanism given in Ref. [11] (see the Supporting Information). In the present work we implemented an HO_2-forming pathway and the reaction of HO_2 with O_3. The potential general relevance of this reaction sequence, exemplified in a study on isoprene ozonolysis,[18] was discussed earlier.[14]

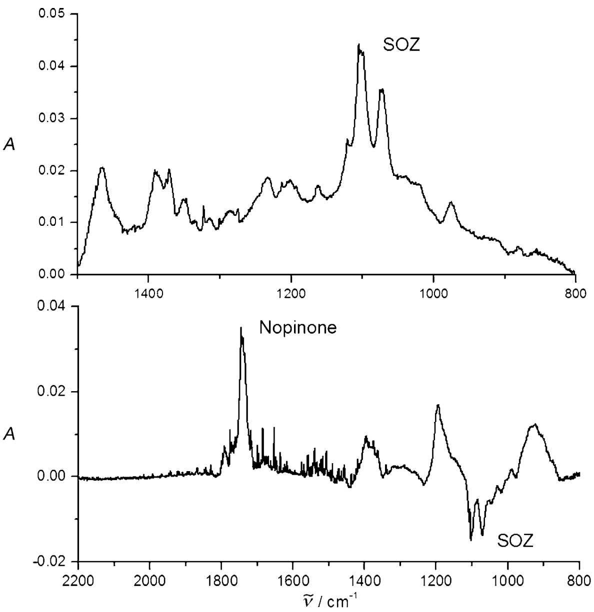

Figure 1. IR product spectra from the ozonolysis of β-pinene (30 ppm β-pinene, 9 ppm ozone, 298 K, here the pressure is 1 bar). Top: Product spectrum in the fingerprint region with SOZ band (experiment without SO_2). Bottom: Difference IR spectrum generated from a similar experiment with 3 ppm SO_2 (experiment with SO_2 minus experiment without SO_2); proof of additional nopinone formation and suppression of SOZ formation is indicated.

It is immediately clear from the experiment that SO_2 consumption and nopinone formation are directly coupled, as assumed in the model. This suggests that reaction (8) is indeed responsible for nopinone formation. Similar to this result is the finding of Taatjes et al.[8] for the reaction of $CH_3CHOO + SO_2$. Here the formation of SO_3 (unambiguously detected by its mass and ionization energy at 12.81 eV) was found to be correlated with SO_2 consumption. However, the experiments by Taatjes and co-workers were restricted to low pressure.

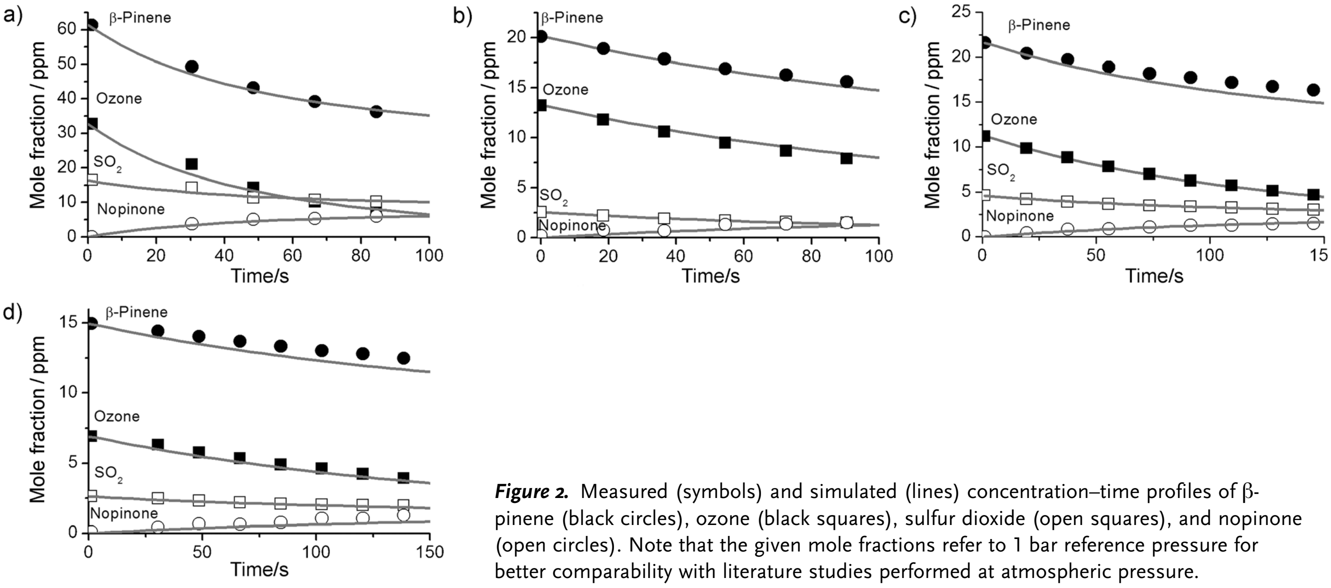

Figure 2. Measured (symbols) and simulated (lines) concentration–time profiles of β-pinene (black circles), ozone (black squares), sulfur dioxide (open squares), and nopinone (open circles). Note that the given mole fractions refer to 1 bar reference pressure for better comparability with literature studies performed at atmospheric pressure.

Vereecken and co-workers discussed the formation of stable CI-SO_2 adducts for larger CIs and higher pressures.[19] Together with the results found for 1 bar in our previous work,[11] it is clear now that such a stabilization cannot be observed in β-pinene ozonolysis on the timescale of our experiment. The stabilized large CIs react with SO_2 to form SO_3 and nopinone. The yield of formed nopinone relative to consumed SO_2 was determined to be at least 80%. This analysis is based on the concentration determinations from the time-resolved IR measurements (see Figure 2) and the evaluation of a series of difference spectra for experiments with and without SO_2. In the difference spectrum the small contribution of nopinone formed without SO_2 in reaction (4) is cancelled out, the positive C=O stretching feature (see Figure 1, bottom panel) is fully consistent with a nopinone spectrum.[11] A similar analysis showed that the consumption of SO_2 relative to ozone is (30 ± 5)%, indicating a sCI yield of roughly 30% at 450 mbar. For the kinetic simulations shown in Figure 2 the rate coefficient for reaction (8) is assumed to be $k = 4\times10^{-11}\ \mathrm{cm^3\,s^{-1}}$. When the value is reduced by a factor of 10 or greater, the consumption rate of SO_2 is significantly underestimated (Figure 3). However, the situation is different if the rate of unimolecular isomerization of CI-1 is assumed to be ten times slower ($k = 5\ \mathrm{s^{-1}}$, see discussions in Refs. [11,17,20]) than predicted in Refs. [11,17]. In this case a much broader range of values for reaction (8) is compatible with the observed SO_2 concentration profiles.

The new, time-resolved experiments in this work support our previous indirect findings that reaction (8) is as fast as the reactions of CH_2OO and CH_3CHOO with SO_2.[7,8] Significant additional evidence that the kinetic assumptions in our model (which are the general assumptions about gas-phase ozonolysis in all models) are correct would be obtained if we could detect the sCIs, which are formed in reaction (5) and are subsequently consumed in reaction (7) (or in reaction (8) in the presence of SO_2). CI-2 in particular is very stable (estimated unimolecular rate coefficient of $1\ \mathrm{s^{-1}}$ compared to $50\ \mathrm{s^{-1}}$ for CI-1[17]).

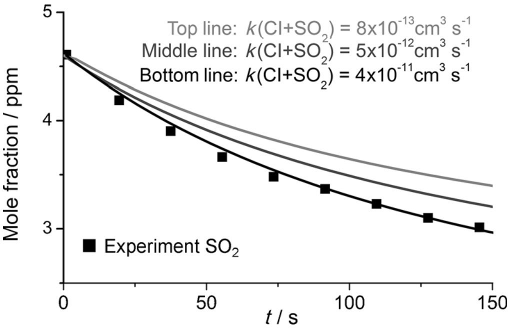

Figure 3. Comparison of the experimental SO_2 concentration profile (22 ppm β-pinene, 11 ppm ozone, 4.7 ppm SO_2) with those predicted based on different assumptions regarding the rate coefficient of reaction (8). Experiments were performed at (450 ± 10) mbar and (298 ± 0.5) K.

The following features of the concentration–time profiles of CI-1 and CI-2 are predicted by the model. Increasing the initial reactant concentrations raises the initial formation rate of the CIs and their peak concentration in the simulation. At high initial concentrations, the consumption of sCIs by the bimolecular reaction with carbonyl compounds (in our case formaldehyde) becomes important because they are formed in a 1:1 ratio with the CIs. It is this “contamination” of the reaction mixture with sCI scavengers, characteristic of the ozonolysis reaction, which limits the maximum sCI concentrations by raising the initial reaction rate. However, at the beginning of the reaction the concentration of carbonyl compounds is zero and sCI concentrations, in particular of CI-2, are predicted in a range that should allow detection if a strong absorption band is available (Figure 4a). The intense absorption feature below 950 $\mathrm{cm^{-1}}$ predicted for CI-1 and CI-2 is a promising band for sCI detection (Figure 4b, 3LYP/6-311+G(2d,2p) level of theory, scaling factor of harmonic frequencies: 0.97, Gaussian 09 package[21]).

To eliminate undesired background signals we performed two types of experiments: one with only alkene and O_3 in the

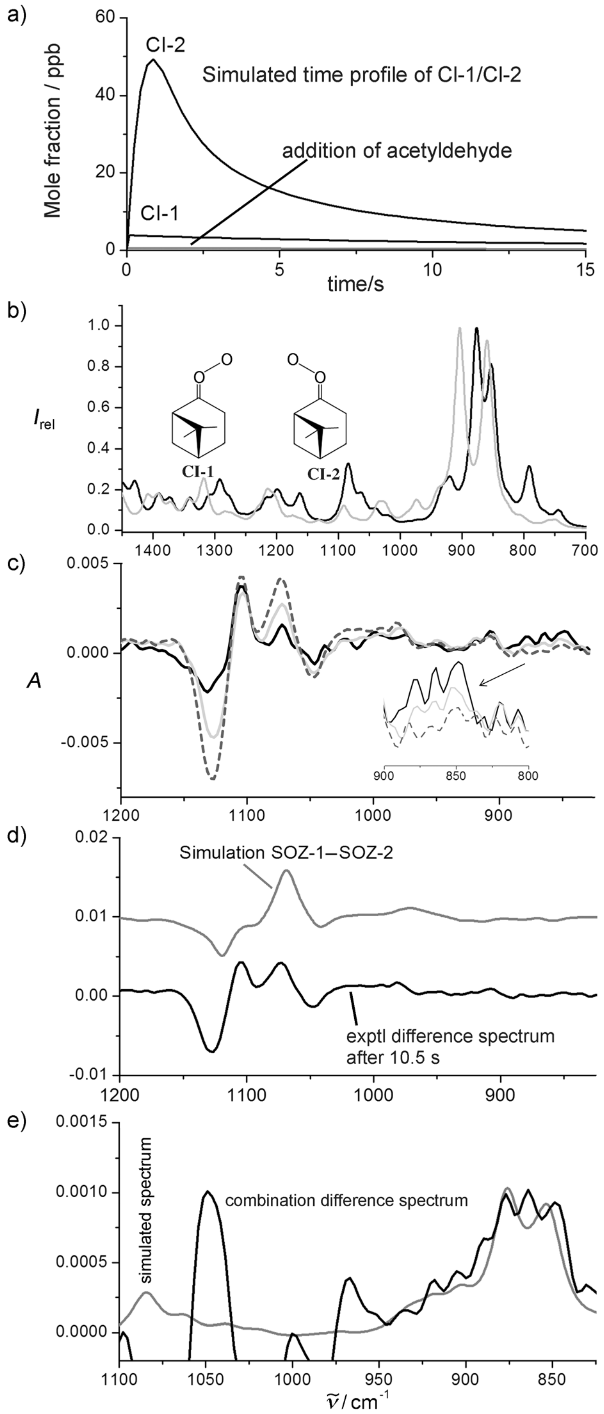

Figure 4. Detection of CIs at the beginning of β-pinene ozonolysis. a) Simulated time profile (100 ppm β-pinene, 30 ppm ozone) of CI-1 and CI-2 (lowest line: CI-1 + CI-2, presence of acetaldehyde). b) Simulated IR spectra of CI-1 (gray) and CI-2 (black). c) Experimental time-resolved IR difference spectra (absence minus presence of 30 ppm acetaldehyde) in the fingerprint region taken in the time windows 0.5–2.5 s (black line), 5–7 s (gray line), and 9.5–11.5 s (dotted line) after the opening of valves to premixing chambers. d) Comparison of the experimental with predicted IR difference spectra for SOZ-1 (CI-1,2 + HCHO) and SOZ-2 (CI-1,2 + CH_3CHO). e) Comparison of the predicted IR spectrum of CI-1/CI-2 (15 %/85 %) with experimental IR double difference spectrum (first (0.5–2.5 s) minus last (9.5–11.5 s) time-resolved IR difference spectrum of Figure 4c).

initial mixture and a second one, in which acetaldehyde, a “foreign” aldehyde was added to the reactants (see Section 5.2 in Ref. [6]). The addition of acetaldehyde drastically reduced the sCI concentrations in the initial phase (Figure 4a, lowest trace). The second change of the product spectrum caused by the addition of acetaldehyde is that a methyl group is added in the SOZ, which is now formed by the reaction sCI + $CH_3CHO \rightarrow$ SOZ-2 instead of sCI + HCHO $\rightarrow$ SOZ-1. Ideally, the difference spectrum in the fingerprint region for these two experiments should show two features: first, the signature of CH_3 substitution in the strong SOZ band around 1100 cm^{-1} and second, an absorption below 950 cm^{-1} (CI-1 and CI-2), which fades in the first 10–15 s. We performed six identical experiments with and without acetaldehyde. The averaged IR difference spectra for three time windows (0.5–2.5, 5–7, and 9.5–11.5 s) are shown in Figure 4c. As expected based on the kinetic and spectroscopic simulation, a transient absorption below 950 cm^{-1} is observed, which agrees with the predicted concentration–time profile of CI-2. Moreover, the IR difference spectrum of the fingerprint region in the last time window is consistent with the predicted difference spectrum between only two species, namely SOZ-1 and SOZ-2 (Figure 4d). This finding is independent of the choice of certain SOZ diastereomers (see the Supporting Information). These observations demonstrate how effectively the elimination of ozonolysis reaction products in the IR difference spectrum works, and they show that the experiment is highly sensitive to CI chemistry.

The prominent IR signature of the large CIs is extracted by taking a further difference spectrum between the first and the last time window. Its envelope below 950 cm^{-1} agrees well with the predicted IR spectrum for CI-2 and best for a mixture of 15 % CI-1 and 85 % CI-2 (Figure 4e; see also the Supporting Information for the results for different experimental conditions and quantum chemistry approaches). The dominance of CI-2 over CI-1 is caused by the much higher stability of CI-2 (Figure 4a). The intensity maxima of the large CIs (ca. 865 cm^{-1}) are shifted to lower frequencies compared to the maximum absorption of CH_2OO at 908 cm^{-1}, recently reported by Lee and co-workers,[10] which is in agreement with harmonic and anharmonic frequency predictions on various levels of theory (see the Supporting Information).

To summarize, we have collected independent spectroscopic proof (band shape and position of the strong O–O stretching feature) and kinetic evidence (consistency with predicted concentration profile, unambiguous and time-resolved detection of SOZ-1,2 as direct reaction products) that the transient absorption below 950 cm^{-1} indeed corresponds to the large C_9-CIs formed during β-pinene ozonolysis. Alternative explanations such as isomers of CI-1 and CI-2 (a vinylhydroperoxide and a dioxirane, see Ref. [17]) are difficult to completely rule out in ozonolysis experiments, but they seem very unlikely owing to the many kinetic and spectroscopic constraints. The exceptionally strong absorption feature below 900 cm^{-1} is characteristic only for the CIs, not for their isomers (see Figures S6 and S7 in the Supporting Information). Minor interferences with other product bands, however, cannot be excluded.

An important point is that the presence of the stable CI-2 in detectable concentrations at the start of the experiment is predicted by the kinetic model used in this work. It is based on literature data and validated by the time-resolved concentration profiles shown in Figure 2. Therefore, the observation of the transient sCI absorption represents a direct experimental confirmation that our general assumptions about the (gas-phase) ozonolysis mechanism are correct.[6,22–24] Moreover, a complementary experimental method for the direct detection of large biogenic sCIs is provided that may help to overcome some limitations of the present photolytic precursors for larger sCIs (e.g. stabilization of RI$-O_2$ adducts and the low vapor pressures of diiodoalkanes). Because of its connection to ozonolysis, the method is in principle applicable to all sCIs. However, further improvements in detection sensitivity have to be made for using sCI concentration–time profiles (as a function of reactant addition) for accurately determining rate coefficients.

In the present study we have demonstrated that Criegee intermediates, formed during the ozonolysis reaction in the gas phase, can be detected by FTIR spectroscopy. Furthermore, the results fill some crucial knowledge gaps by unambiguously showing that large biogenic sCIs can effectively produce SO_3 in the reaction with SO_2. This reaction is probably as fast as the directly measured results for small CIs indicate.[7,8] The remaining uncertainty is mainly related to the rates of unimolecular isomerization of sCIs, which determine their atmospheric lifetimes and thus their availability for bimolecular reactions.[11,13,17,20]

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Keywords: Criegee intermediates · IR spectroscopy · ozonolysis · β-pinene · tropospheric sulfur chemistry

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[1] P. Paasonen, A. Asmi, T. Petäjä, et al., *Nat. Geosci.* **2013**, *6*, 438–442.
[2] M. Sipilä, T. Berndt, T. Petäjä, D. Brus, J. Vanhanen, F. Stratmann, J. Patokoski, R. L. Mauldin, A.-P. Hyvärinen, H. Lihavainen, M. Kulmala, *Science* **2010**, *327*, 1243–1246.
[3] J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., Wiley-Interscience, New York, **1998**.
[4] R. A. Cox, S. A. Penkett, *Nature* **1971**, *230*, 321–322.
[5] S. Hatakeyama, H. Akimoto, *Res. Chem. Intermed.* **1994**, *20*, 503–524.
[6] R. Criegee, *Angew. Chem.* **1975**, *87*, 765–771; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 745–752.
[7] O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, C. A. Taatjes, *Science* **2012**, *335*, 204–207.
[8] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. K. W. Mok, D. L. Osborn, C. J. Percival, *Science* **2013**, *340*, 177–180.
[9] J. D. Fenske, A. S. Hasson, A. Ho, S. E. Paulson, *J. Phys. Chem. A* **2000**, *104*, 9921–9932.
[10] Y.-T. Su, Y.-H. Huang, H. A. Witek, Y.-P. Lee, *Science* **2013**, *340*, 174–176.
[11] P. T. M. Carlsson, C. Keunecke, B. C. Krüger, M.-C. Maaß, T. Zeuch, *Phys. Chem. Chem. Phys.* **2012**, *14*, 15637–15640.
[12] R. L. Mauldin III, T. Berndt, M. Sipilä, P. Paasonen, T. Petaäjä, S. Kim, T. Kurtén, F. Stratmann, V.-M. Kerminen, M. Kulmala, *Nature* **2012**, *488*, 193–196.
[13] M. Boy, D. Mogensen, S. Smolander, L. Zhou, T. Nieminen, P. Paasonen, C. Plass-Dülmer, M. Sipilä, T. Petäjä, L. Mauldin, H. Berresheim, M. Kulmala, *Atmos. Chem. Phys.* **2013**, *7*, 3865–3879.
[14] J. L. Wolf, S. Richters, J. Pecher, T. Zeuch, *Phys. Chem. Chem. Phys.* **2011**, *13*, 10952–10964.
[15] P. T. M. Carlsson, J. E. Dege, C. Keunecke, B. C. Krüger, J. L. Wolf, T. Zeuch, *Phys. Chem. Chem. Phys.* **2012**, *14*, 11695–11705.
[16] R. Winterhalter, P. Neeb, D. Grossmann, A. Kolloff, O. Horie, G. K. Moortgat, *J. Atmos. Chem.* **2000**, *35*, 165–197.
[17] T. L. Nguyen, J. Peeters, L. Vereecken, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5643–5656.
[18] T. L. Malkin, A. Goddard, D. E. Heard, P. W. Seakins, *Atmos. Chem. Phys.* **2010**, *10*, 1441–1459.
[19] L. Vereecken, H. Harder, A. Novelli, *Phys. Chem. Chem. Phys.* **2012**, *14*, 14682–14695.
[20] T. Berndt, T. Jokinen, R. L. Mauldin III, T. Petaäjä, H. Herrmann, H. Junninen, P. Paasonen, D. R. Worsnop, M. Sipilä, *J. Phys. Chem. Lett.* **2012**, *3*, 2892–2896.
[21] Gaussian 09, Revision A02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., **2009**.
[22] M. Olzmann, E. Kraka, D. Cremer, R. Gutbrod, S. Andersson, *J. Phys. Chem. A* **1997**, *101*, 9421–9429.
[23] D. Johnson, G. Marston, *Chem. Soc. Rev.* **2008**, *37*, 699–716.
[24] N. M. Donahue, G. T. Drozd, S. A. Epstein, A. A. Presto, J. H. Kroll, *Phys. Chem. Chem. Phys.* **2011**, *13*, 10848–10857.