Spatial Separation of the Conformers of Methyl Vinyl Ketone

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Methyl vinyl ketone (C3H6O) is a volatile, labile organic compound of importance in atmospheric chemistry. We prepared a molecular beam of methyl vinyl ketone with a rotational temperature of 1.2(2) K and demonstrated the spatial separation of the s-cis and s-trans conformers of methyl vinyl ketone using the electrostatic deflector. The resulting sample density was 1.5(2) × 108 cm−3 for the direct beam in the laser ionization region. These conformer-selected methyl vinyl ketone samples are well suited for conformer-specific chemical reactivity studies such as in Diels-Alder cycloaddition reactions.

I. INTRODUCTION

Methyl vinyl ketone (MVK, 3-butene-2-one, C3H6O) is the simplest α, β-unsaturated ketone and an important oxygenated volatile organic compound. MVK results from many sources such as vehicle exhaust13, biomass burning14, and the ozonolysis of isoprene4. As a primary first-yield product of isoprene oxidation in earth’s atmosphere15, MVK remains in the gas phase and is highly reactive16. As a result, MVK has an important impact on the photochemical activity in the boundary layer, especially in forested areas17, and contributes to the destruction of ozone due to its fast reaction with hydroxyl radicals and methylglyoxal18. The atmospheric lifetime of MVK is ~10 days due to its fast reaction with hydroxyl radicals under atmospheric conditions19. On the other hand, in the troposphere isoprene reacts with hydroxyl radicals and ozone molecules leading to a significant yield of MVK20, which is important for the formation of secondary organic aerosols and the overall NOx cycle21. Moreover, MVK is a candidate for prototypical pericyclic reactions, such as the Diels-Alder (DA) cycloaddition22.23.

The ultraviolet absorption24, microwave17,19, and infrared20,23 spectra of MVK provided evidence for a mixture of s-cis and s-trans MVK conformers and showed that s-trans MVK is more stable than s-cis MVK. Recently, the high-resolution rotational (7.5–18.5 GHz24, 540–6500 cm−125) and infrared spectra (540–6500 cm−125) of MVK were reported. By combining experimental data and high-level quantum-chemistry calculations, the relative energy of s-trans MVK and s-cis MVK was determined as 164 ± 30 cm−125, yielding an equilibrium mixture of approximately 69% s-trans MVK and 31% s-cis MVK at room temperature25,26.

The reactivity of different conformers may vary significantly27,28. Neutral molecules can be manipulated in the gas-phase using the electrostatic deflection technique29, which was demonstrated for the separation of individual quantum states30,31, conformer32,33, or molecular clusters34,35. This separation can be exploited for the investigation of the specific chemical reactivities of individual molecular species36,37.

Here, we demonstrate the preparation of a cold and dense molecular beam of MVK and the spatial separation of the s-cis and s-trans conformers using the electrostatic deflector. Furthermore, we determine the density of the produced cold samples. The spatially separated conformers of MVK could be used for non-species-specific experiments, e.g., conformer-specific reactivity studies38 or ultrafast structural imaging experiments39,40.

II. EXPERIMENTAL METHODS

The experimental setup was described previously25,41. A homebuilt gas handling system with a rotating high-pressure cylinder was added to fully and permanently mix MVK (Sigma-Aldrich, 99%, used without further purification) and helium, see Figure S1 in the supplementary information. The reservoir was filled with 2 ml of MVK, de-aired down to ∼10−2 mbar, and the MVK vapor was mixed with helium gas at 20 bar. The gas mixture was supersonically expanded through a cantilever piezo valve42 operated at a repetition rate of 20 Hz. Helium seed gas was used for best rotational cooling and minimal longitudinal dispersion of the beam and correspondingly high beam density in the interaction region for the planned conformer-specific chemical-reaction experiments. Two skimmers, placed 55 mm (∅ = 3 mm) and 365 mm (∅ = 1.5 mm) downstream of the valve were used to collimate the molecular beam, which was then directed through the electrostatic deflector43 before passing through a third skimmer (∅ = 1.5 mm) 562 mm downstream of the nozzle. MVK was ionized by a femtosecond laser with a wavelength centered at ~800 nm and a pulse duration of 45 fs (full-width at half maximum, FWHM) that was focused to 44(4) µm (FWHM, ω0 = 37(3) µm)
in the interaction region by a \( f = 500 \) mm lens. The resulting ions were detected by a two-plate time-of-flight (TOF) mass spectrometer (MS).

III. RESULTS AND DISCUSSION

MVK is a liquid at room temperature and condenses on the sample reservoir walls, resulting in fast demixing of the prepared gas mixtures and corresponding fast decays of the MVK density in the molecular beam. Demixing was avoided through rotation of the sample reservoir (vide supra) and Figure 1 shows the resulting stability of the MVK signal following 20 h of sample rotation. Under these conditions the sample density was stable over a few hours and it decreased to 70 % over four days.

The normalized experimental vertical molecular beam profiles of MVK for different backing pressures of 2, 4, 6, and 8 bar are shown in Figure S5 in the supplementary information. The full width of the direct molecular beam (0 kV) is 2 mm, determined by the skimmers and the distance between the third skimmer and ionization point. The deflected beam (10 kV) is deflected upward by \( \approx 0.8 \) mm when a pressure of 2 bar is applied to the piezo valve. Increasing the pressure to 4 bar, 6 bar, and 8 bar the deflection of the beam increases to \( \approx 1.0 \) mm, \( \approx 1.1 \) mm, and \( \approx 1.1 \) mm, respectively, which is due to the correspondingly lower rotational temperature of these beams.

Figure 2 a shows the experimental and simulated molecular beam profiles of MVK seeded in 8 bar of helium for deflector voltages of 0 V and 10 kV. The mass spectrum of the direct (0 kV) and deflected (10 kV) molecular beam are shown in Figure S4 in the supplementary information. The spectrum of the deflected beam mainly contains signals from the MVK parent ion \( M^+ \) (\( m/z = 70 \)) and from fragment ions [M-CH\(_2\)=CH\(]^+ \) (\( m/z = 43 \)) and [M-CH\(_3\)]\(^+ \) (\( m/z = 55 \)).

Solid and dotted lines in Figure 2 a show simulated spatial profiles using the molecular parameters and calculations detailed in the supplementary information. The effective dipole moments of the rotational states of \( s\text{-trans} \) are larger than ones of \( s\text{-cis} \) and, therefore, \( s\text{-trans} \) deflects further than \( s\text{-cis} \). Assuming a thermal distribution of the population of rotational states, the best fit for the profile of MVK in Figure 2 was obtained for a rotational temperature of 1.2(2) K. The deflection and simulation profiles of MVK seeded in different pressures of helium are shown in Figure S3 in the supplementary information.

Although no full separation was possible, \( s\text{-trans} \) MVK was deflected more than \( s\text{-cis} \) MVK. The fractional contributions of the conformers across the vertical beam profile are shown in Figure 2 b assuming the same excitation and ionization cross-sections for the two conformers. A beam of \( s\text{-trans} \) conformer with a purity higher than 90 % was obtained for vertical molecular-beam positions \( y \geq 1.9 \) mm.

The MVK sample densities in the experiments were estimated based on a strong-field ionization model. Assuming an instrument sensitivity of 50 % for the MCP detector, the asymptotic slope of an integral ionization signal with respect to the natural logarithm of peak intensity can be expressed as \( S = q \pi \sigma^2 f \), where \( q \)
IV. CONCLUSION

We demonstrated the use of a rotating-sample reservoir for the production of a dense and cold molecular beam of MVK with stable molecular densities over more than a day and a rotational temperature of 1.2(2) K. This allowed for the spatial dispersion and partial separation of the s-cis and s-trans conformers of MVK using the electrostatic deflector. The achieved direct-beam density in the detection zone was experimentally determined to be 1.5(2) × 10⁸ cm⁻³.

We plan to exploit these conformer-selected MVK samples for reactivity studies, e.g., with the ions of MVK (self-reaction), methyl vinyl ether, and further dienophile cations, to investigate the mechanism and conformational specificities of ionic Diels-Alder (DA) cycloaddition reactions. Furthermore, the reactivity of the conformers in reactions with neutral atmospheric molecules, such as OH, would be extremely interesting for atmospheric chemistry applications.

SUPPLEMENTARY INFORMATION

See the supplementary material for a schematic of the gas panel, the direct and deflected molecular beam profiles of MVK for different backing pressures, the mass spectra obtained in the direct and the deflected molecular beams, the rotational constants and dipole moments of the MVK conformers, their Stark energies, and the deflection and simulation profiles of MVK seeded in helium of different pressures.

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