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Miranda F. Shaw, David L. Osborn, Meredith J. T. Jordan, and Scott H. Kable J. Phys. Chem. A, Just Accepted Manuscript • Publication Date (Web): 24 Apr 2017 Downloaded from http://pubs.acs.org on April 25, 2017

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Infrared Spectra of Gas-Phase 1- and 2-Propenol Isomers

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Abstract

Fourier transform infrared spectra of isolated 1-propenol and 2-propenol in the gas-phase have been collected in the range of 900-3800 cm⁻¹, and the absolute infrared absorption cross sections reported for the first time. Both *cis* and *trans* isomers of 1-propenol were observed with the *trans* isomer in greater abundance. *Syn* and *anti* conformers of both 1- and 2propenol were also observed, with abundance consistent with thermal population. The FTIR spectrum of the smaller ethenol (vinyl alcohol) was used as a benchmark for our computational results. As a consequence, its spectrum has been partially re-assigned resulting in the first report of the *anti*-ethenol conformer. Electronic structure calculations were used to support our experimental results and assign vibrational modes for the most abundant isomers; *syn-trans*-1-propenol and *syn*-2-propenol.

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Introduction

Enols have become increasingly recognised as important reactive intermediates in atmospheric^{1,2} and combustion²⁻⁶ chemistry, and have recently been implicated as precursors to atmospheric carboxylic acids. ^{1,7,8} Known sources of enols are aldehydes⁹⁻¹¹ and ketones,¹² which are an abundant organic constituent of the troposphere and themselves intermediates in the photo-oxidation of volatile organic compounds (VOCs).¹³ There are two photochemical routes for gas-phase carbonyls to form enols: the well-known Norrish Type II mechanism, and the more recently reported photo-tautomerisation. Both reactions begin with absorption of actinic UV light via an ($\pi^* \leftarrow n$) electronic transition to the S_1 surface.

The Norrish Type II reaction (NT-II) is one of the two major photolysis reactions of longer chain aldehydes and ketones.¹⁴ Following excitation to the excited surfaces, the carbonyl oxygen atom abstracts a hydrogen atom from the γ -carbon, and subsequent bond cleavage yields the enol plus an alkene. This process occurs on both the singlet and triplet surfaces.¹⁵ Scheme 1 shows the concerted NT-II reaction for butanal.¹⁶



Scheme 1. Norrish Type II reaction of butanal.

The NT-II reaction occurs in competition with the Norrish Type I reaction (NT-I, homolytic C–C σ -bond cleavage adjacent to the carbonyl) and a minor cyclisation reaction.

Photo-tautomerization can occur if the molecule returns to a vibrationally-excited, electronic ground state (S_0) via internal conversion (IC) from S_1 , or intersystem crossing (ISC) from T_1 . Isomerization to the enol is then possible via a tight transition state on S_0 .¹⁰ An example is shown in Scheme 2, for the photo-tautomerization of acetaldehyde, the quantum yield for which is both pressure and wavelength dependent.¹¹



Scheme 2. Phototautomerisation of acetaldehyde to vinyl alcohol.

The importance of this process has been increasingly recognized in recent years, given the high atmospheric concentrations of small carbonyls such as acetaldehyde, propanal and acetone. In addition, the NT-II reaction is not possible in these smaller carbonyls because they lack γ -hydrogens.

The smallest enol, vinyl alcohol (ethenol) is a tautomer of acetaldehyde, and has been studied in detail. However, there is no spectroscopic data in the gas-phase for the tautomers of propanal and acetone: 1- and 2-propenol. Matrix infrared spectra of 2-propenol¹⁷ and some larger substituted enols¹⁸⁻²⁰ have been obtained, but studies of propenols have been limited to mass spectrometry²¹ and NMR.²² To the best of our knowledge, vibrational spectroscopy of enols in the gas phase is limited to the spectrum of vinyl alcohol.^{23,24} Infrared spectroscopy is an especially useful technique for the observation of short-lived, gas-phase enols, as they can be readily observed *in situ*, at a range of photolysis wavelengths and pressures, including simulated atmospheric conditions. We have previously used this technique to study the synthesis and spectrum of vinyl alcohol, and now report the gas phase infrared spectra of 1and 2-propenol, produced by the NT-II reactions of \Box 2-methylbutanal and 2-pentanone respectively, summarised in Schemes 3a and 3b respectively.



Scheme 3. Synthesis of (a) 1-propenol, and (b) 2-propenol.

Experimental

The experimental procedure for photolysis and collection of Fourier transform infrared (FTIR) spectra have been described previously.¹¹ In brief, experiments were conducted in a 12.4×12.4 cm Teflon-coated, cross-shaped stainless steel cell. The cell was placed in an evacuated FTIR spectrometer (Bruker IFS 66 v/S) and aligned such that the IR beam propagated along one axis through polished KBr windows, while monochromatic UV photolysis laser pulses propagated along the perpendicular axis through fused silica windows.

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FTIR scans were taken using a liquid-nitrogen-cooled HgCdTe detector in the range of 820 – 3800 cm^{-1} . The detector is not sensitive to radiation below 820 cm⁻¹. The cell was evacuated and flushed with N₂ between experiments. No photochemical deposits on the fused silica windows were observed during these experiments. 2-Methylbutanal and 2-pentanone liquids (Aldrich, $\geq 99.5\%$) were purified by several freeze–pump–thaw cycles and delivered directly to the evacuated cell as neat vapour. The pressure of the gas, typically 2 – 10 torr, was monitored using two MKS Baratron gauges. At the instrumental resolutions used (0.25 and 1 cm⁻¹), pressure broadening does not contribute to the spectral line shape. Photolysis was conducted using a tunable OPO laser pumped by a pulsed Nd:YAG laser at a 10 Hz repetition rate. The photolysis beam (5 mm diameter, 3 – 5 mJ/pulse of UV light) was reflected through the cell four times. We do not expect multiphoton absorption to be important in the unfocused beam.

Computational Methods

Geometry optimisations and frequency calculations were performed with a range of computational methods that have been reported to accurately reproduce experimental infrared spectra.²⁵ Vibrational frequencies, including anharmonic corrections for MP2 and DFT methods, were evaluated for MP2,²⁶ CCSD(T),^{27,28} and the B3LYP, ²⁹ BLYP,³⁰ B97-1,³¹ and EDF2³² functionals, with a 6-31+G(d,p)³³ basis set. Harmonic frequencies were adjusted according to literature scaling factors.³⁴

To examine isomer ratios and reaction mechanisms, geometry minima and transition states were optimised with B3LYP/6-31+G(d,p), and single point energy calculations performed on optimised structures with CCSD(T) and a cc-pVTZ³⁵ basis set, with additional diffuse functions on carbon and oxygen atoms. Reported energies include zero-point vibrational energy corrections.

Frequency calculations using the EDF2 functional were performed with the QChem software package,³⁶ the Gaussian 09³⁷ suite was used for all other optimisation and frequency calculations, and Molpro³⁸ used for CCSD(T) single point energy calculations. PGOPHER³⁹ was used to simulate the rotational structure of predicted infrared bands.

Results and Discussion

Ethenol (Vinyl Alcohol)

We have previously published the gas-phase infrared cross sections of vinyl alcohol (VA), from the NT-II reaction of butanal.¹¹ A comparison of our previously published experimental spectrum,¹¹ those from the literature, ^{23,24} and the predicted spectra from several computational methods was first used to benchmark an appropriate level of theory to accurately predict the VA spectrum. Because the vibrational modes arising from the alkene and hydroxy functional groups are very similar for VA and the larger enols, the most accurate method could then be used to aid assignment of spectra for 1- and 2-propenol.

Vinyl alcohol has two geometric minima, with the hydroxyl group in a *syn* or *anti* orientation with respect to the double bond. The *syn* geometry is energetically favoured by 4.2 kJ mol⁻¹ at the CCSD(T)//B3LYP level of theory. In this orientation there is a weak interaction between the hydroxyl hydrogen and the relatively electron rich C=C bond; no such interaction is possible in the *anti* geometry. The barrier for this σ -bond rotation, however, is relatively small (15-20 kJ mol⁻¹).⁴⁰

Figure 1 shows the FTIR spectrum of VA measured by us previously.¹¹ The spectrum is dominated by the COH in-plane bending (v₉) and C=C stretching (v₅) modes. The experimental spectrum shows a splitting of both of these bands, which has been attributed to Fermi resonance between (v₉) and the (v₁₄+v₁₅) combination band at 1082 cm⁻¹, and between (v₅) and the 2v₁₃ overtone at 1626 cm⁻¹.^{41,42} Rotational constants from the most intense bands have been analysed previously and found to correspond to the lower-energy *syn* conformer.²⁴ The observed VA bands have been assigned accordingly throughout the literature.^{23,24}

The vibrational frequencies for *syn*-VA were calculated with a range of density functionals and *ab initio* methods listed earlier, and compared to experimental literature frequencies for *syn*-VA (excluding v_8 , *vide infra*). Mean absolute deviations (MADs) between calculated and literature frequencies ranged from 10 to 40 cm⁻¹. Of the methods tested here, the best results were seen for B3LYP and B97-1 anharmonic frequencies, with MADs of only 9.7 and 10.7 cm⁻¹, respectively.

As shown in Table 1, the observed band at 1260 cm^{-1} had previously been assigned as the v_8 fundamental, ^{23,24} one of the COH bending modes. However this band was poorly predicted by every computational method, for both wavenumber and intensity. It appears to be one of the stronger bands in the experimental spectrum (see Figure 1), but is calculated to have near-zero intensity.

Figure 2 shows the displacement vectors for v_8 and v_9 for both the *syn* and *anti* conformers. Both modes involve a COH bending motion but v_8 causes only a small change in dipole moment for *syn*-VA, whereas v_9 results in the high intensity band at 1118 cm⁻¹. For *anti*-VA, it is v_8 that has the larger change in dipole moment and corresponding high intensity. The calculated frequency for v_8 of *anti*-VA is 1233 or 1254 cm⁻¹ from B3LYP and B97-1 respectively, which is very close to the observed 1260 cm⁻¹ band in the experimental spectrum. We therefore conclude, on the basis of our anharmonic calculations, that the experimental gas-phase spectrum contains both the *syn* and *anti* VA conformers, and the observed band at 1260 cm⁻¹ is in fact the strong transition involving v_8 of the *anti* conformer.

It follows that the actual v_8 band of *syn*-VA is instead the observed band at 1300 cm⁻¹, which had previously been assigned as v_7 . From the low calculated intensity and weak signal in the matrix, it is likely that the actual v_7 band is too weak to be easily observed in the gas-phase. By reassigning the v_7 and v_8 bands in the gas-phase spectrum of *syn*-VA, this also resolves the relatively large differences in these vibrations between the gas-phase and matrix spectra. This difference in assignments of v_7 and v_8 had been previously noted, but were ascribed to matrix effects rather than to the presence of an additional conformer.²⁴

We have calculated the relative populations of the two VA conformers from their Boltzmann weight at 300 K, using the calculated energy difference of 4.2 kJ mol⁻¹ at the CCSD(T)//B3LYP level of theory. This analysis assumes room temperature distributions of both isomers. Implicit in this assumption is that collision-induced thermalisation occurs on a much faster time scale than our experiments.⁷ At equilibrium, 85% of VA is calculated to be in the syn conformation and 15% is in the anti conformation. This ratio is consistent with the microwave spectrum obtained by Rodler *et al*,⁴³ in which an energy difference of 4.5 kJ mol⁻¹ was predicted by the ratio of signal intensities. Our predicted syn and anti room temperature infrared spectra of VA using this ratio are shown below our experimental, gas-phase spectrum in Figure 1. The rotational band countours are determined by the symmetries of the vibrations, with in-plane modes appearing as A/B-type hybrid bands and the out-of-plane modes appearing as C-type bands. Comparing the syn- and anti- contributions to the predicted spectrum, note the comparable intensities of the v_1 OH bands despite the minor 15% mole fraction of the anti- conformer. The width and intensity of the observed spectrum in the isolated OH stretch region agrees well with the 85:15 population ratio and the predicted infrared intensities, offer further support for our assignments. Overall, Figure 1 shows very

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good agreement for both the calculated frequencies and the ratio of VA conformers. We have therefore used similar methods to predict and interpret the propenol spectra.

1-Propenol

2-Methylbutanal was irradiated at 295 nm. This wavelength was chosen for the large UV absorption cross section,⁴⁴ and because the NT-I and NT-II processes listed below occur with very high efficiency at this wavelength, resulting in few minor and secondary products. Figure 3 shows the FTIR spectrum after 5 minutes of irradiation of 2-methylbutanal, where absorptions due to 2-methylbutanal have been subtracted. The major products observed were 1-propenol, ethene, CO, formaldehyde and butane, with a minor amount of propanal and 3,4-dimethylhexane as described by reactions (R1) to (R6).

2-methylbutanal +
$$hv \rightarrow H\dot{C}O + CH_3CH_2\dot{C}HCH_3$$
 (NT-I) (R1)

2-methylbutanal +
$$hv \rightarrow C_2H_4 + CH_3CH=CHOH (NT-II)$$
 (R2)

 $2 \text{ H\dot{C}O} \rightarrow \text{ CO} + \text{H}_2\text{CO}$ (R3)

$$H\dot{C}O + CH_3CH_2\dot{C}HCH_3 \rightarrow CO + CH_3(CH_2)_2CH_3$$
(R4)

$$2 \text{ CH}_3\text{CH}_2\dot{\text{C}}\text{H}\text{CH}_3 \rightarrow \text{ CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \qquad (\text{R5})$$

$$CH_3CH=CHOH \rightarrow CH_3CH_2CHO$$
 (tautomerization) (R6)

The contributions from all stable photoproducts and products of bimolecular reactions, other than 1-propenol, were quantified and subtracted using scaled reference spectra for these pure compounds acquired at the same resolution as the photochemical spectrum and under similar conditions. With the relatively low yields and pressures involved (<100 mTorr of products), absorbance and number density are related linearly as described by the Beer-Lambert Law. The residual signal in the FTIR spectrum is shown in Fig. 4, which we argue below can be assigned to 1-propenol isomers.

There are four geometry minima for 1-propenol: *cis* or *trans* about the C=C bond, and *syn* or *anti* with respect to the CCOH dihedral angle (see Fig. 4). We calculated anharmonic IR frequencies and harmonic intensities of all four isomers using the B3LYP and B97-1 functionals that were benchmarked against ethenol above. The *syn* and *anti* conformers are

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analogous to those discussed for ethenol, and we have assumed that a 300 K thermal population determines their relative abundance. The *syn* conformers of each structural isomer are again lower in energy and expected to account for 81% of the *trans* isomer and 62% of the *cis* isomer abundance. Steric interference from the *cis* methyl group reduces the stability of its *syn* conformer, decreasing its ratio of *syn:anti* compared to either trans-1-propenol or vinyl alcohol. This effect is even more pronounced in polar solvent, where the *anti*-conformer apparently becomes the dominant stereochemistry of *cis*-1-propenol, as observed by NMR.²²

We have not made any assumptions about the relative abundance of the *cis* or *trans* isomers, because we calculate the *cis-trans* interconversion barrier to be 284 kJ mol⁻¹, and hence the two isomers should not interconvert at 300 K. Their abundance likely reflects the dynamics of their formation, not their thermodynamic stabilities. Therefore the relative abundance of each isomer was adjusted to best match the experimental spectrum, with a 1:9 ratio of *cis:trans* reproducing experiment very well. Figure 4 compares the experimental spectrum to the four predicted spectra, weighted to best reproduce the experimental spectrum.

The *syn-trans* isomer of 1-propenol accounts for the majority of the activity in the spectrum; we were able to assign most of the observed bands by comparing to the calculated anharmonic frequencies, which are listed in Table 2. All ground state propenol isomers have C_s point group symmetry. The fundamental modes are comprised of 16 in-plane vibrations with A' symmetry, and 8 out-of-plane vibrations with A'' symmetry. The A'' symmetries correspond to C-type bands, and A' symmetries result in A-type, B-type or A/B hybrid bands, depending on the orientation of the transition moment with respect to the two in-plane inertial axes. These rotational band contours were simulated using the rotational constants calculated at the B3LYP/6-31+G(d,p) level of theory. Where possible, the observed rotational band contours were used to confirm the vibrational assignments. The five overlapping C-H stretching bands from 2900 – 3000 cm⁻¹ were left unassigned. The calculated frequencies of the other isomers are available in Supporting Information.

Figure 5 shows the most intense bands of 1-propenol at higher resolution. Although Figure 5a and Figure 5b are dominated by the most abundant isomer, the OH stretching band in 5c strongly suggests overlapping A/B-hybrid type bands, with a similar appearance to the OH stretching region of the VA spectrum. The OH stretch in the *syn* conformers of both VA and *trans*-1-propenol is red-shifted due to the attractive interaction between the OH group and the double bond. The OH in the anti conformer does not have this interaction, and therefore vibrates at a slightly higher frequency. The sharp features in Figure 5c are observed from $3493-3744 \text{ cm}^{-1}$, with a spacing that increases steadily from 6.7 cm⁻¹ to 8.7 cm⁻¹. However,

we were unable to assign the carrier of this spectrum from the rotational constant (assuming a linear molecule). The spectral resolution is insufficient for Doppler broadening to assist in the assignment.

We explored the relative abundance of *cis* and *trans* isomers as a kinetic effect, determined by the height of the transition state of the NT-II reaction. The γ -hydrogen transfer to the oxygen atom creates a "chair-like" six-membered ring, which shows a small reduction in energy if the methyl group is in an equatorial rather than axial position. Figure 6 shows our calculation of the transition state structures and the preceding geometries as they occur on the T_1 surface, for the (*S*) enantiomer of 2-methylbutanal. The aldehyde and transition state structures exist in both (*R*) and (*S*) stereoisomeric forms but produce identical, achiral products. An energy difference in the barrier height of 4 to 6 kJ mol⁻¹ between the equatorial vs. axial saddle point structures was consistent for several levels of theory. A 5 kJ mol⁻¹ difference in barrier height produces an approximately 7-fold difference in rate of reaction over the barrier (assuming a constant pre-factor). This ratio is quite consistent with the observed 9-fold enhancement of the *trans* isomer over the *cis* isomer.

2-Propenol

The photolysis of 2-pentanone was conducted and analyzed as described above for 2methylbutanal. As well as ethene, 2-propenol and acetone, the major products arising from the NT-I process were biacetyl, ethenone (ketene), and alkanes, as described by Equations (R7) to (R11). 2-Pentanone can also undergo a variation of the NT-I reaction in which cleavage occurs on the other side of the carbonyl, producing $CH_3CH_2CH_2\dot{C}O$ and $\dot{C}H_3$ radicals. This reaction was unlikely to be occurring as the calculated barrier is 16 kJmol⁻¹ higher than the barrier for (R7), and we did not see evidence of methane or ethane molecules that would arise from methyl radicals.

2-pentanone +
$$hv \rightarrow CH_3CO + CH_3CH_2CH_2$$
 (NT-I) (R7)

2-pentanone + $hv \rightarrow C_2H_4 + H_2C=C(OH)CH_3$ (NT-II) (R8)

 $2 \text{ CH}_3 \dot{\text{CO}} \rightarrow \text{ CH}_3 \text{COCOCH}_3$ (R9)

$$CH_3\dot{C}O + CH_3CH_2\dot{C}H_2 \rightarrow H_2C = C = O + CH_3CH_2CH_3$$
(R10)

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 $2 \text{ CH}_3\text{CH}_2\dot{\text{CH}}_2 \rightarrow \text{CH}_3(\text{CH}_2)_4\text{CH}_3 \tag{R11}$ $H_2\text{C}=\text{COHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3 \text{ (tautomerization)} \tag{R12}$

After subtraction of reference spectra for all stable products in (R7) - (R12), other than 2-propenol, the spectrum in Fig. 7 was obtained, which we attribute to 2-propenol.

2-Propenol also has *syn* and *anti* conformations with the *syn* (OH towards C=C) being lower energy, analogous to vinyl alcohol and 1-propenol. With a calculated energy difference of 5.8 kJ mol⁻¹, over 90% of the enol is expected to be in the *syn* conformation at equilibrium at 300 K. The simulated spectrum with this ratio of conformers is shown in Figure 7 and again shows good agreement with the experimental spectrum. Like 1-propenol, the in-plane, *A*' symmetry vibrations produce A/B-hybrid contours and the out-of-plane, *A*" symmetry vibrations produce C-type bands, distinctive due to their very strong Q-branch K-stacks. As was seen for the other enols, the most intense band in the predicted *anti* spectrum is the COH bending mode, which appears ~100 cm⁻¹ higher than the equivalent syn band. It is therefore likely that the broad band observed from 1260 - 1330 cm⁻¹ contains both the anti COH bending mode, and some of the weaker CH bending modes from the *syn* conformer. The absorbance of the 2-propenol spectrum was too low to distinguish any weaker bands from the *anti* conformer.

Table 3 lists the observed and calculated frequencies, as well as the observed frequencies of matrix isolated 2-propenol.¹⁷ B97-1 anharmonic frequencies are shown for the CH and OH stretching modes as these gave slightly better agreement with experiment than did B3LYP for this molecule. This region shows relatively poor agreement with the matrix values. An additional band was observed in the matrix spectrum at 2835 cm⁻¹ and assigned as v₅, whereas our assigned v₂ band at 3110 cm⁻¹ was not reported for the matrix spectrum. The rest of the spectrum shows good agreement between the present gas-phase spectrum and that collected in the matrix. Argon-matrix and gas-phase spectra typically differ by 1-10 cm⁻¹, and up to 20 cm⁻¹ for OH stretching bands,⁴⁵ which is consistent with the data in Table 3. The gas-phase enol had previously been identified only by reduced transmittance at 3628 cm⁻¹,¹² which is well within the range of the broad absorption band that we see here (approximately 3610 – 3660 cm⁻¹).

There are some key differences in the spectra of 1- and 2-propenol. 2-Propenol shows a more intense C-H bending mode at 1386 cm⁻¹, whereas the COH bend at 1185 cm⁻¹ is both less intense and shifted 70 cm⁻¹ higher than the corresponding band in 1-propenol. An additional

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weak band is observed at 1606 cm⁻¹, attributed to Fermi resonance between the $2v_{20}$ overtone and the high intensity C=C stretching band. The v_{20} fundamental is below our observed wavenumber range, but the overtone is estimated to be in the range of 1600 - 1640 cm⁻¹ using the calculated and matrix values. Intensity sharing in the Fermi resonance may also explain why the intensity of the experimental C=C stretching band is lower than in the simulated spectrum; the relative intensities are otherwise well predicted. Fermi resonance is seen in this region in the spectrum of vinyl alcohol, with the equivalent $2v_{13}$ overtone. The active vibration in both cases is the out-of-plane "wag" of the terminal methylene group which is not possible for 1-propenol.

Quantitative absorption cross-sections

One of the motivations for the present research is to measure the quantum yield of photochemical processes that produce the 1- and 2-propenol molecules, for example via the NT-II pathway or by photo-tautomerization from a 3-carbon carbonyl molecule. The measurement of quantitative concentrations and therefore quantum yields requires knowledge of the infrared absorption cross-section for each enol, which is reported below.

The number density of enol produced in the NT-II reaction was calculated using the measured changes in number density of the parent, and of the ethene product, which is formed in a 1:1 stoichiometric ratio with the enol. Two kinetic models were used: a simpler model where the concentration of the parent, methylbutanal, is assumed to remain unchanged through the course of the experiment and a more complex model where the slow decrease in parent concentration is explicitly included. The observed loss of parent was consistently 2-5% for all photolysis wavelengths and the inferred cross-section for the enol varies by only 1% between the complex and simple model. Therefore, only the simple kinetic model is explained here; the derivation of the more complex model can be found in Supplementary Material.

Because the amount of parent photolyzed is only a small percentage of the total, the NT-II reactions (R2) and (R7) can be considered pseudo-zeroth order, with an effective rate constant of k_{1} ':

$$k_1' = k_1 [parent] \tag{K1}$$

$$[E] = k_1' t \tag{K2}$$

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where [E] is the ethene concentration. Under this assumption, [E] rises linearly with time during photolysis, consistent with the experimental data in Fig. 8a for 2-methylbutanal and Figure 8b for 2-pentanone photolysis.

Although propenol (P) is produced at an equal rate to ethene (E), it also undergoes a wallcatalyzed, first order decay to the keto form (propanal or acetone), with rate constant k_2 , throughout the duration of the experiment. The overall change in propenol concentration can therefore be described by the rate equation K3, which integrates to K4:

$$\frac{d}{dt}[P] = \frac{d}{dt}[E] - k_2[P] \tag{K3}$$

$$[P] = \frac{k_1'}{k_2} \left[1 - e^{-k_2 t} \right] \tag{K4}$$

The rate constant for enol production, k_1' , is equal to the fitted, approximately linear rate of increase in ethene over time.

The rate constant for the tautomerization reaction (R6 or R12), k_2 , was found by observing the time-dependent decrease in absorbance of the major enol bands in the ten minutes following irradiation (after the laser was turned off), and fitting these to a first order exponential decay. Both rate constants depend on experimental factors such as photolysis wavelength, laser power, and gas pressure for k_1 , and cell coating for k_2 .

Figure 8 shows the measured, experimental number densities for (a) 1-propenol and (b) 2-propenol, including the kinetic fit to equations K2 and K4.

The wall-catalyzed tautomerization described by k_2 was considerably faster for 2-propenol than either 1-propenol or vinyl alcohol. Rather than a slow decay of the enol signal as we saw for the other enols, 2-propenol was completely absent from the spectrum in less than a minute. Fig. 8 shows this rapid loss of enol during irradiation, where the rate of decay quickly reaches the rate of production, and we see a small, constant amount of enol after the first two minutes. Nevertheless, the rate constant for the decay of 2-propenol was found by fitting Equation (K4) to the integrated absorbance of the C=C band between $1570 - 1630 \text{ cm}^{-1}$ (shown in Fig. 8b), and the OH stretching band at $3610 - 3670 \text{ cm}^{-1}$. These two regions were chosen because there was no overlap with bands from other species.

From the calculated enol number densities, the Beer-Lambert Law was used to calculate the IR absorption cross-sections of 1- and 2-propenol at 1 cm⁻¹ resolution, as shown in Fig. 9. We estimate the total uncertainty in 1-propenol absorption cross-sections to be 10-15%. Despite

the much faster decay of 2-propenol due to tautomerization, the reasonable S/N ratio in the spectrum produced a quantitative IR absorption cross-section for 2-propenol with uncertainty that we estimate at 20%.

The enol IR cross-section and the decay mechanism for 1-propenol (R6) was also checked by recording the time dependence of the propanal (keto-tautomer) spectral signature. The propanal number density was determined by the same method as for other species, i.e. measuring a reference spectrum at known pressure. The sum of the number densities of propanal and 1-propenol was always within ~5% of the measured ethene number density at all wavelengths, pressures and irradiation times. This conservation of keto/enol species provided additional evidence that the calculated cross-section of 1-propenol is accurate, and that the enol does indeed decay via tautomerization to its keto form.

Finally, we also compared the integrated experimental cross sections to the calculated intensities for the most intense and least overlapping bands of the most abundant conformers – the OH stretching, C=C stretching, and COH bending modes. The average ratio of calculated intensities to integrated cross sections for these vibrational modes was 0.84 for *syn-trans*-1-propenol and 0.68 for *syn*-2-propenol. We consider these values to indicate quite good agreement given that we only included one isomer in the calculated intensity, and the likely error in both experimental cross sections and calculated intensities.

Conclusions

We have measured quantitative infrared spectra of gas-phase 1- and 2-propenol and assigned the major constituents as *syn-trans*-1-propenol and *syn*-2-propenol respectively. We have also clarified the assignment of the gas-phase ethenol spectrum, which includes contributions from *anti*-ethenol. These enol spectra will assist photochemistry studies of enol-producing carbonyls, including both longer chain molecules that undergo the Norrish Type II reaction, and smaller, abundant molecules such as acetaldehyde, acetone and propanal that can tautomerize to their enol isomer. Although these enols react with the walls of our vessel and decay back to their keto form within 1-10 minutes under low-pressure laboratory conditions, their tropospheric lifetime has been estimated from tens of minutes to hours depending on the surrounding conditions,^{46,47} allowing competitive OH initiated oxidation to organic acids to occur.⁸

We have reassigned part of the vinyl alcohol infrared spectrum, identifying a contribution from the minor *anti*- conformer in this spectrum. Finally, our experimental spectrum of 1-

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propenol is most consistent with a 1:9 ratio of *cis:trans* isomers. We provide an explanation for this population ratio based on the Norrish Type II photodissociation mechanism after intersystem crossing to the lowest triplet state, in which a higher energy transition state for formation of *cis* relative to *trans* controls the dominance of the *trans* isomer produced.

Supporting information:

Digitized spectra, reporting both absorbance and absorption cross section, versus wave number. Derivation of the complete kinetics scheme, and the calculated vibrational frequencies for all isomers of 1- and 2-propenol.

Acknowledgements:

The Australian authors acknowledge financial support of the Australian Research Council (grant number DP160101792). MFS acknowledges an Australian Postgraduate Award. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, who provided the experimental apparatus and support of DLO.

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TABLES:

Table 1. Observed and predicted (anharmonic, B3LYP/6-31+G(d,p)) vibrational frequencies for vinyl alcohol.

			sy	n-VA	an	ti-VA
	Literature expt gas / cm ⁻¹ a,b	Expt Ar matrix / cm ⁻¹ c	Calc. freq (cm ⁻¹)	Calc. intensity (Debye ² Å ² amu^{-1})	Calc. freq (cm ⁻¹)	Calc. intensity (Deby $e^2 Å^2$ amu^{-1})
ν_1	3634 m	3620 s	3609	0.69	3681	1.65
ν_2	3122 w	-	3112	0.25	3129	0.19
ν_3	-	-	3050	0.15	3041	0.00
v_4	-	-	2999	0.17	3023	0.67
ν_5	1663 ^d m	1662 ^d vs	1669	1.88	1677	2.59
ν_6	1412 w	1409 w	1405	0.23	1400	0.00
v_7	1300 w	1326 w	1324	0.21	1323	0.01
ν_8	1260 m	1300 m	1284	0.02	1234	5.23
v 9	1118 ^d vs	1121 ^d s	1103	4.86	1116	0.30
ν_{10}	948 w	943 w	946	0.32	941	1.30
v_{11}	-	-	486	0.30	480	0.09
v_{12}	960m	971 m	962	0.85	940	0.68
v_{13}	817 s	813 s	816	1.87	844	1.61
ν_{14}	699 w	698 w	693	0.04	699	0.46
v_{15}	-	413 s	379	2.52	351	2.18

(a) Experimental intensities described by w=weak, m=medium, s=strong, vs=very strong.

(b) Gas phase frequencies from Koga *et al*²⁴ and Joo *et al*²³(c) Matrix frequencies from Hawkins *et al*⁴¹ and Rodler *et al*.⁴² (d) Experimental frequencies corrected for Fermi resonance perturbations, as described in Koga *et al*²⁴ and Rodler *et al*.⁴²

 v_1

 ν_2

 v_3

 v_4

 v_5

 ν_6

 v_7

 v_8

V9

 ν_{10}

 ν_{11}

 ν_{12}

 v_{13}

 v_{14}

 v_{15}

 v_{16}

 v_{17}

 v_{18}

 v_{19}

 v_{20}

 v_{21}

v22

 v_{23}

 v_{24}

247

173

			••••••		
ıer	ncies.				
	Calc. freq	Obs. freq	Band	Sym.	Mode description ^(b)
	$/ {\rm cm}^{-1}$	$/ {\rm cm}^{-1}$	type ^(a)	(C_s)	-
	3615	3639	A/B	A'	O-H stretch
	3078	3080	(B)	A'	alkene C-H stretch
	2952	2955	(A/B)	A'	alkene C-H stretch
	2949	-	(B)	A'	IP CH ₃ C-H stretch
	2898	2888	(A)	A'	OOP CH ₃ all C-H sym stretch
	1692	1684	A/B	A'	C=C stretch
	1464	1467	(B)	A'	CH ₃ H-C-H bend (scissors)
	1395	1400	(B)	A'	CH ₃ def. (umbrella)
	1351	1362	А	A'	IP alkene C-H bend
	1307	1311	А	A'	IP both alkene C-H bend
					IP C-O-H bend, alkene C-H
	1232	-	(A)	A'	bend
	1105	1108	А	A'	C-O stretch, C-O-H bend
	1083	-	(A)	A'	IP C-O-H bend, CH3 C-H bend
	919	915	(A/B)	A'	CH ₃ wag
	536	-	(B)	A'	IP C-C-C-O bend
	297	-	(A)	A'	IP C-C-C bend
	2919	2932	(C)	A"	OOP CH ₃ C-H antisym. stretch
	1443	-	(C)	A"	CH ₃ C-H OOP bend
	1039	-	(C)	A"	CH ₃ rock
	927	932	С	A"	OOP alkene C-H bend
	785	-	(C)	A"	OOP alkene C-H bend
	355	-	(C)	A''	OOP O-H bend

Table 2. svn-trans-1-Propenol observed and calculated B3LYP/6-31+G(d,p) anharmonic frequ

(a) No parentheses: calculated and observed. In parentheses: calculated only, as the experimental peak is too weak or obscured.

(C)

(C)

A"

Α"

OOP O-H bend

CH₃ torsion

(b) IP = in plane, OOP = out of plane.

-

-

	Calc. freq / cm ⁻¹	Obs. freq / cm ⁻¹	Matrix freq ^(a) / cm ⁻¹	Band type ^(b)	Sym type (C _s)	Mode description
v_1	3638*	3642	3622 w	A/B	A'	O-H stretch
v_2	3106*	3110	2992 w	(A/B)	A'	CH ₂ asym stretch
V3	3000*	3014	2979 w	(A)	A'	CH ₂ sym stretch
v_4	2988*	2977	2950 w	(B)	A'	IP CH ₃ C-H stretch
V 5	2899*	2902	2835 w	(A)	Α'	CH ₃ all C-H sym stretch
V 6	1676	1678	1673 w	A/B	A'	C=C stretch
V 7	1460	1462	1467 m	(B)	Α'	OOP CH ₃ bend (scissors)
v_8	1424	-	-	(A/B)	A'	CH ₂ bend (scissors)
V9	1386	1386	1379 m	(B)	A'	_{CH3} (umbrella), CH ₂ scissor
V ₁₀	1323	1317	1331 w	(B)	A'	C-O-H bend, C-O stretch
v ₁₁	1171	1185	1181 s	A/B	A'	C-O-H bend
V ₁₂	1006	1001	1002 m	(B)	A'	IP CH ₃ rock
V ₁₃	967	-	963 w	(B)	A'	IP CH ₂ C-H rock
V ₁₄	849	-	849 w	(B)	A'	IP C-C stretch
V ₁₅	491	-	478 w	(A/B)	A'	IP CH ₂ -C-OH bend
V16	388	-	-	(B)	A'	IP C-C-C bend
V ₁₇	2938*	2949	2921 w	(C)	A''	OOP CH ₃ C-H asym stretch
V ₁₈	1433	1435	1439 w	С	A''	OOP CH ₃ bend
V19	1048	-	1050 w	(C)	A''	OOP C-C-C bend
V20	794	-	822 w	(C)	A''	OOP CH ₂ wag
V ₂₁	695	-	697 w	(C)	A''	CH ₂ torsion
V ₂₂	495	-	494 w	(C)	A''	OOP C-C-C bend
V ₂₃	420	-	395 s	(C)	A''	OOP O-H bend
V24	218	-	-	(C)	A''	CH ₃ torsion

Table 3. 2-Propenol observed, literature and calculated anharmonic frequencies.

* v₁- v₅, v₁₇ from B97-1.

(a) Literature matrix values from Zhang *et al.*¹⁷

(b) No parentheses: calculated and observed. In parentheses: calculated only, as the experiment is too weak or obscured.

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Figure 1. Experimental and simulated VA spectra. The experimental band marked with an asterisk is discussed in the text. The colored traces show calculated B3LYP/6-31+G(d,p) anharmonic spectra of *syn:anti* conformers in an 85:15 ratio. OOP=out of plane, IP=in plane, FR=Fermi resonance, v = stretching mode, $\delta =$ bending mode. The perturbing species for the FR are indicated as assigned in previous work.²³



Figure 2. COH bending modes for syn and anti VA.



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Figure 3: FTIR spectrum of all major photoproducts from 295 nm irradiation of 2-methylbutanal. Some less abundant species are not labelled.

FTIR spectroscopy of propenols



Figure 4. Simulated and experimental spectra of 1-propenol. Rotational contours were simulated in PGOPHER, using vibrational origins, rotational constants, and dipole derivatives from anharmonic B3LYP/6-31+G(d,p) calculations. The relative fraction of each isomer is discussed in the text.



Figure 5. Highest intensity bands of 1-propenol at 0.25 cm⁻¹ resolution. (a) COH bend at 1108 cm⁻¹ (b) C=C stretch at 1684 cm⁻¹ (c) OH stretching bands at 3639 cm⁻¹ and 3693 cm⁻¹. Major contributing isomers/conformers are shown.

FTIR spectroscopy of propenols



Figure 6. NT-II reaction on the T_1 surface. Energies are reported in kJ mol⁻¹ and are relative to the S_0 minimum, calculated at CCSD(T)/aug'-cc-pVTZ//B3LYP/6-31+G(d,p).



Figure 7. Simulated and experimental spectra of 2-propenol. The simulated spectra contain vibrational origins from electronic structure calculations, and rotational contours from PGOPHER,³⁷ using calculated rotational constants and dipole derivatives.



Figure 8. Fitted and predicted number densities of ethene and enol in the photolysis of (a) 2-methylbutanal, and (b) 2-pentanone, using Equations (K2) and (K4).

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Figure 9. Absolute infrared absorption cross-sections for 1- and 2-propenol at 1 cm⁻¹ resolution. No signal from either molecule was observed between 1800 – 2800 cm⁻¹.



















132x224mm (300 x 300 DPI)







75x38mm (300 x 300 DPI)