Supplemental Information: The ozonolysis of isoprene in a cryogenic buffer gas cell by high resolution microwave spectroscopy

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1 Product Ratios with CP-FTMW

The predicted line intensity for one mole of molecules as reported by Bunker and Jensen is [1]:

$$I_{(f \leftarrow i)} = \frac{8\pi^3 \nu_{if} N_A e^{-E_i/kT}(1 - e^{-h\nu_{if}/kT})S_{if}}{(4\pi\epsilon_0)3hc^2 Q_{rot}} \tag{1}$$

where ν_{if} is the frequency in Hz, N_A is Avogadro's number, S_{ij} is the intrinsic line strength for a given transition, E_i is the lower state energy, ϵ_0 is the vacuum permittivity constant, and Q_{rot} is the rotational partition function. The intrinsic line strengths are calculated from simulations in PGOPHER. All products (ap-MACR, ap/sp-MVK, $CH_2{=}O$, and HCOOH) were included in a mixture simulation, and line strengths were exported based upon best fit rotational parameters from Pickett, or the literature as cited below (see Table 2). [2,3]. Rearranging we take the ratio of N_1 to N_2:

$$\frac{N_1}{N_2} = \frac{e^{-E_2/kT}(1 - e^{-h\nu_2/kT})\nu_2 S_2 I_1 Q_{rot1}}{e^{-E_1/kT}(1 - e^{-h\nu_1/kT})\nu_1 S_1 I_2 Q_{rot2}} \tag{2}$$

We have calculated Q_{rot} at 6.68 K, with rigid-rotor levels being calculated by diagonalization followed by partition function calculation by direct summation:

$$Q_{rot} = \sum_k exp(-E_k/k_B T) \tag{3}$$

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A number of lines and their respective constants required for this calculation at 6.68 K are summarized in Table 1. In each calculation the molecules were assumed to be in thermal equilibrium with the measured temperature of the cell, which presumably leads to introduction of systematic error. Although there are many potential approaches to account for differences in instrument response from frequency to frequency, here we have simply validated lines for internal consistency. The ratio of one line to another for the same given species should be 1, and those that deviated more than 20% from this result were thrown out of analysis on account of changes in instrument response.

Transition	Frequency (MHz)	E_i (MHz)	I (arb)	S_{if}
ap-methyl vinyl ketone ($3_{12} \rightarrow 2_{11}$)	23481.9751	28981.2681	0.957	5.664812
ap-methyl vinyl ketone ($4_{04} \rightarrow 3_{13}$)	24423.4119	44508.8043	0.654	3.212288
sp-methyl vinyl ketone ($4_{04} \rightarrow 3_{13}$)	22386.1804	45010.2005	1.12	7.845789
sp-methyl vinyl ketone ($4_{23} \rightarrow 4_{14}$)	25870.9216	70321.429	0.264	2.013059
ap-methacrolein ($3_{03} \rightarrow 2_{02}$)	20950.7446	21795.4726	4.12	6.890302
ap-methacrolein ($3_{21} \rightarrow 2_{20}$)	23259.2774	42125.8447	2.44	3.975087
formic acid ($1_{01} \rightarrow 0_{00}$)	22471.1914	0	3.09	0.644960
formaldehyde ($2_{11} \rightarrow 2_{12}$)	14488.4766	456785.1436	24.4	1.510203

Table 1: Sample values used in the calculation of MACR/MVK from 2:1 ozone to isoprene ozonolysis data at 4% overall reagent in argon, 298 K and 5 Torr.

Species	Q_{rot}	μ / D	Ref
ap-methyl vinyl ketone	28.537	a: 2.53 ± 0.03	Foster[4], Wilcox[5]
		b: 1.91 ± 0.04	Foster[4], Wilcox[5]
sp-methyl vinyl ketone	27.786	a: 0.66	Wilcox[5]
		b: 3.19	Wilcox[5]
ap-methacrolein	28.601	a: 2.67 ± 0.015	Suzuki[6]
		b: 0.84 ± 0.04	Suzuki[6]
$trans$-formic acid	6.316	a: 1.391 ± 0.005	Kim[7], Willemot[8], Davis[9]
		b: 0.26 ± 0.04	Kim[7], Willemot[8], Davis[9]
formaldehyde	2.141	a: 2.33167 ± 0.00001	Bocquet[10]

Table 2: Rotational partition functions (at 6.68 K) and dipole moments used in the branching ratio analysis in the ozonolysis of isoprene.

2   Reagents and Ozone Purification

Isoprene (Aldrich 99% containing <1000 ppm p-tert-butylcatechol as inhibitor) was diluted to 2% in argon (UHP). Flow rates were chosen to maximize throughput, and therefore pressure, while minimizing heat load on the cold cell. Authentic samples (isoprene, MVK, MACR, and formaldehyde) were used for comparison to the spectra obtained with the isoprene / ozone mixture. Neat samples of MVK (Aldrich 99% containing 0.5% hydroquinone and 0.1% acetic acid as stabilizer) and MACR (Aldrich, 95%) were individually studied by injection through a mass flow controller at 1 sccm. Formaldehyde (Aldrich containing 10-15% methanol

as stabilizer, 37 wt. % in H_2O) solution was directly injected via a capillary tube into the buffer gas cell at 2 μL per minute. All samples were used without further purification.

The standard procedure for pure ozone generation involved the following: High purity O_2 (99.999% Middlesex grade 5.0) was passed through an ozone generator (Welsbach) at 5 psig. The output (conversion efficiency roughly 1.5%) at 2 standard liters per minute was directed into a cold silica gel trap at -78 °C. Argon was then passed through the trap into a collection vessel and filled to atmospheric pressure, with the first few seconds of argon flow vented off to remove residual O_2. To establish the ozone concentration, ozone absorption was measured with the output of a 255 nm UV LED (3 mW) through a small concentration cell equipped with sapphire windows and a silicon photo-diode (Thorlabs PDA10A). Depletion of ozone in the cylinder at such low dilutions (typically 5% O_3 in Ar) was negligible on the timescale required for data acquisition.

3   Additional Estimations

The helium density inside the buffer gas cell is estimated based upon effusive, steady state flow conditions with a mass balance formula[11]: $n_{He} = \frac{4f}{Av_{He}}$, for a flow rate f (7 sccm), cell aperture area (2.85 cm^2) and the mean He velocity. Mean velocity $v_{He} = \sqrt{\frac{8k_BT}{\pi m_{He}}}$ is 188 m s^{-1} at 6.68 K, and 1 sccm is equivalent to approximately 4.48 $\times 10^{17}$ atoms s^{-1}. Therefore He cell density can be estimated as:

$$n_{He} = \frac{4(4.48 \times 10^{17} \text{atoms/s})(7\text{sccm})}{(2.85\text{cm}^2)(1.92 \times 10^4)} \tag{4}$$

or approximately 2×10^{14} He atoms cm^{-3}. From Houston $et.$ $al.$, If the density of molecules of type 2 (He) is n_2*=n_{He}, then the number of collisions one molecule of type 1 will experience with molecules of type 2 per unit time is[12]:

$$Z_{2,1} = \pi b_{max}^2 < v_r > n_2* \tag{5}$$

With b_{max} representing the approximate impact parameter, or the sum of the collision partner radii. The relative velocity $< v_r >$ of He with products can be calculated by the following:

$$< v_r >= (\frac{8kT}{\pi\mu})^{1/2} \tag{6}$$

Assuming the approximate average mass of methyl vinyl ketone, methacrolein, and isoprene $etc.$ is on the order of 70 g/mol (isoprene 68 g/mol), then the reduced mass for an He / isoprene collision is $m_1m_2/(m_1 + m_2)$ is 3.78 amu. There are 1.66054 $\times 10^{-27}$ kg/amu, so the reduced mass for this collision is

6.29 $\times 10^{-27}$ kg. This leads to an average relative velocity $< v_r >$ of 193 m/s between He and isoprene at 6.68 K. If we assume a hard sphere collisional cross section of He of 1.4 $\times 10^{-10}$ m, and roughly ten times that for the large collision partner, we get an approximate $b_{max} = 15 \times 10^{-10}$ m. Plugging this into equation 5, we get $Z_{2,1}$= 2.73 $\times 10^5$ collisions/s. Within reason we can assume that product/He collisions occur roughly once every 10 μs, depending on the hard sphere radius and molar mass assumed for the collision partner with He. Given the assumption that larger molecules are collisionally thermalized within roughly 20 - 100 collisions[13], we can safely assume thermalization of hot molecules in the buffer gas cell occurs within 1 ms or less. Lastly, we can estimate the residence time, or the time reagents are allowed to mix before entering the buffer gas cell, based upon the following: $\tau = LA/Q$ With flow rate Q (15 sccm, 96% argon), L total alumina and PFA tube length (115 cm), and A the cross sectional area at the exit of the tube (0.017 cm^2), we derive a rough estimate of $\tau = 10$ s for residence time.
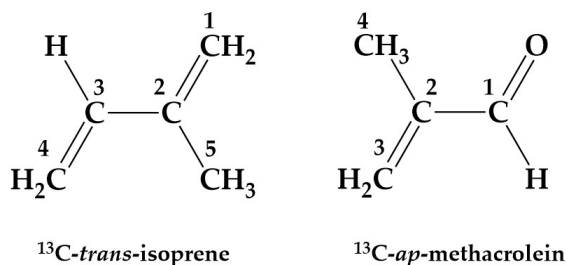
4 Line lists and constants

Figure 1: Isotopic labeling of ^{13}C-*trans*-isoprene for Tables 3 and 4, and ^{13}C-*ap*-methacrolein for Tables 5 and 6.

Table 5: Observed lines (MHz) for the normal and isotopically substituted ^{13}C ap-methacrolein.

Transition	^{12}C	^{13}C 1	^{13}C 2	^{13}C 3	^{13}C 4
$1_{01} \to 0_{00}$	7368.3	7325.4	7351.7	7217.3	7307.9
	7368.5	7325.7	7352.2	7217.6	7308.2
$1_{11} \to 0_{00}$	11577.3	11503.0	11572.6	11408.2	11245.7
$2_{02} \to 1_{01}$	14426.8799	14342.1631	14397.4915	14139.0076	14278.4424
	14427.3071				
$2_{11} \to 1_{10}$	16173.9502	16081.2988	16135.0098	15834.5337	16079.4678
	16174.7437	16082.0923	16135.8032	15833.8013	16078.6743
$2_{12} \to 1_{11}$	13299.0112	13220.2148	13272.4609	13035.2783	13153.0151
	13299.2554	13220.3979	13272.7051	13035.5835	13153.2593
$2_{12} \to 1_{01}$	17508.0566	17397.7661	17493.2698	17226.2573	
$2_{11} \to 2_{02}$	7393.6667				
	7394.0667				
$2_{20} \to 2_{11}$	12936.1572	12840.6982			12150.9399

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Table 5: Observed lines (MHz) for the normal and isotopically substituted ^{13}C ap-methacrolein.

Transition	^{12}C	^{13}C 1	^{13}C 2	^{13}C 3	^{13}C 4
	12936.8286	12841.4307			12150.2986
$2_{21} \to 2_{02}$	20020.4443				19014.0356
	20020.8716				19014.4019
$2_{21} \to 2_{12}$		16824.2798	16955.8716	16770.3857	
$3_{03} \to 2_{02}$	20950.5591	20825.3149	20912.2900	20546.6284	20677.1826
	20950.9253	20825.6812	20912.6562	20546.9946	20677.4878
$3_{03} \to 2_{12}$	17869.3848	17769.5312			17865.3564
	17870.1782	17770.3247			17864.5630
$3_{12} \to 2_{11}$	24041.5625	23903.0737	23985.5322		23876.8296
	24042.6611	23904.1724	23986.6309		23876.8296
$3_{13} \to 2_{02}$		22710.0195	22829.7095	22471.4914	22350.7056
$3_{13} \to 2_{12}$	19771.9702	19654.2234	19733.8843	19384.1528	19538.0835
	19772.2754	19654.5996	19734.1895	19384.4580	19538.4497
$3_{21} \to 2_{20}$	23258.6646	23126.7676	23198.7280		23170.1636
	23259.8853	23127.9883	23199.9847		23171.4453
$3_{22} \to 2_{21}$	22104.5508	21975.9497	22055.4175		21923.5815
	22105.3442	21976.7432	22056.2109		21924.3750
$3_{12} \to 3_{03}$	10484.7333				
	10485.8667				
$3_{22} \to 3_{03}$	21174.8633				20260.8618
$3_{21} \to 3_{12}$	12153.3813	12064.5142		12083.0688	
	12153.9307	12065.0635		12083.6182	
$3_{22} \to 3_{13}$	19272.2144	19145.9937	19277.4023		
	19272.7026	19146.4819	19277.8906		
$3_{31} \to 3_{22}$		24639.2798			
$4_{04} \to 3_{13}$	25076.9019	24931.0278		24546.5063	24904.8437
	25076.1694	24931.6992		24547.1777	24905.5151
$4_{13} \to 3_{22}$	20897.0923				
	20899.5337				
$4_{13} \to 4_{04}$	15093.1396	15013.0615	15047.2412		
	15095.2759	15015.2588	15049.4385		
$4_{13} \to 4_{14}$	14083.0688				
	14085.6323				
$4_{14} \to 3_{13}$				25580.1367	25755.0635
				25580.5029	25755.4297
$4_{22} \to 4_{13}$	12284.7900				
$4_{23} \to 4_{04}$	23425.1074	23273.1909			22647.8247
	23425.8398	23273.9233			22648.6182
$4_{23} \to 4_{14}$	22415.0366				21797.5439
	22416.1353				21798.7036
$4_{32} \to 4_{23}$	25569.8828				24353.4521
	25570.1880				24353.6963
$4_{32} \to 5_{15}$			15812.8052		
$5_{14} \to 5_{05}$				20454.9536	
$5_{14} \to 5_{15}$					20667.0508
					20670.4077
$5_{23} \to 4_{32}$			18385.0684		
$5_{23} \to 5_{14}$	13822.1436				
	13822.9980				

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Table 5: Observed lines (MHz) for the normal and isotopically substituted ^{13}C ap-methacrolein.

Transition	^{12}C	^{13}C 1	^{13}C 2	^{13}C 3	^{13}C 4
$5_{32} \rightarrow 5_{23}$	20080.7471				
	20082.3950				
$6_{24} \rightarrow 6_{15}$	17075.8973				
$6_{24} \rightarrow 6_{25}$	13422.0581				
	13425.8423				
$6_{25} \rightarrow 5_{32}$	14807.7393				
	14808.0444				
$6_{33} \rightarrow 6_{24}$	18644.8340				
	18646.1157				
$7_{16} \rightarrow 6_{33}$	15238.4033				
	15238.7085				
$7_{26} \rightarrow 6_{33}$	17270.8740				
	17269.4702				
$9_{36} \rightarrow 9_{37}$	17963.8062				
	17970.2759				

Transition	^{13}C 1	^{13}C 2	^{13}C 3	^{13}C 4	^{13}C 5
$1_{10} \rightarrow 1_{01}$	5623.3333	5679.0000	5631.1333		5435.9333
$2_{11} \rightarrow 2_{02}$		7253.6734			
$2_{02} \rightarrow 1_{11}$		9411.4677			
$3_{12} \rightarrow 3_{03}$	9853.4797	10019.3211	9977.4273		9939.1422
$1_{11} \rightarrow 0_{00}$	11223.8480	11374.9333	11300.2877	11318.3910	11063.0970
$4_{22} \rightarrow 4_{13}$	12308.1665	12417.4194	12305.4810	12606.5674	11838.6780
$3_{21} \rightarrow 3_{12}$	12423.8000	12507.2883	12377.5712	12814.6940	11780.1689
$2_{20} \rightarrow 2_{11}$	13250.8545	13338.3658	13198.8525		12548.7061
$5_{23} \rightarrow 5_{14}$				13490.0513	
$4_{13} \rightarrow 4_{04}$	13902.7100	14172.4854	14135.2539		
$3_{03} \rightarrow 2_{12}$	16440.9519	16776.6714	16731.6667	16190.8484	16845.0284
$2_{12} \rightarrow 1_{01}$	16824.3471	17070.8400	16969.4214	16901.2597	16690.2637
$2_{21} \rightarrow 2_{12}$	16869.8730	17036.9263	16893.3106	17206.4209	16307.6667
$3_{22} \rightarrow 3_{13}$					18488.6279
$4_{13} \rightarrow 3_{22}$		18792.5220			
$5_{32} \rightarrow 5_{23}$	20909.5874				
$4_{23} \rightarrow 4_{14}$	21744.6704		21884.3924	21939.9219	
$3_{13} \rightarrow 2_{02}$	21885.5396		22089.8183		21764.6877
$4_{23} \rightarrow 4_{14}$		22027.9346			21428.4473
$3_{13} \rightarrow 2_{02}$		22216.7500		21953.3405	
$4_{31} \rightarrow 4_{22}$		22742.1069	22492.7173	23387.4316	21298.0762
$4_{04} \rightarrow 3_{13}$	23339.8853	23781.5816	23697.1851	23103.6792	23709.5752
$3_{30} \rightarrow 3_{21}$		24054.3628	23809.0625	24600.7495	22675.9448
$3_{31} \rightarrow 3_{22}$	25036.6066	25246.1353	25009.5630		23973.0029
$4_{32} \rightarrow 4_{23}$		25878.3374	25646.4648		24661.7236
$2_{21} \rightarrow 1_{10}$		28428.7982			
$2_{20} \rightarrow 1_{11}$		30003.5052			
$3_{22} \rightarrow 2_{11}$		34124.6017			
$3_{21} \rightarrow 2_{12}$		39303.2896			

Table 3: Observed lines (MHz) for isotopically substituted ^{13}C *trans*-isoprene. Reported at $\pm$ 50 KHz from a combination of the buffer gas cell and cavity microwave spectrometers.

	A	B	C	D_J	D_{JK}	Lines	σ
^{12}C	8527.045(1)	4175.236(1)	2852.160(1)	0.35(3)	5.40(5)	28	0.90
^{13}C 1	8423.58(1)	4088.959(3)	2800.264(2)		4.8(6)	15	0.43
^{13}C 2	8526.9798(1)	4166.2875(1)	2847.9742(1)	0.279(1)	5.29(1)	24	0.84
^{13}C 3	8465.715(8)	4152.242(3)	2834.573(1)		5.3(6)	17	0.63
^{13}C 4	8526.96(1)	4046.452(6)	2791.443(2)		5.9(7)	12	0.75
^{13}C 5	8249.520(6)	4160.422(3)	2813.594(1)		6.6(4)	17	0.91

Table 4: Rotational (MHz) and centrifugal distortion constants (kHz) for *trans*-isoprene and it's ^{13}C isotopologues, along with the number of lines used in each fit and the error based on weighted averages (σ, kHz).

	A	B	C	D_J	D_{JK}	D_K	δ_J	Lines	σ
^{12}C	8611.99(1)	4403.025(4)	2965.367(4)	0.50(6)	8.2(4)		0.53(2)	36	0.71
^{13}C 1	8555.59(2)	4378.106(6)	2947.412(4)		9(1)	6(2)		21	0.65
^{13}C 2	8612.2766(1)	4391.6604(1)	2960.3510(1)	1.5020(1)			-1.2238(1)	17	0.89
^{13}C 3	8499.13(2)	4308.33(2)	2909.04(1)	-2.8(4)			-2.9(2)	14	0.71
^{13}C 4	8323.21(1)	4385.515(7)	2933.558(7)	0.5(3)	7(1)			21	0.49

Table 6: Rotational (MHz) and centrifugal distortion constants (kHz) for *trans*-methacrolein and it's ^{13}C isotopologues, along with the number of lines used in each fit and the error based on weighted averages (σ, kHz).

References

[1] P. R. Bunker and P. Jensen, *Fundamentals of molecular symmetry*, CRC Press, 2004.

[2] H. Pickett, R. Poynter, E. Cohen, M. Delitsky, J. Pearson and H. Müller, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 1998, **60**, 883–890.

[3] C. M. Western, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2017, **186**, 221–242.

[4] P. D. Foster, V. Rao and R. Curl Jr, *The Journal of Chemical Physics*, 1965, **43**, 1064–1066.

[5] D. S. Wilcox, A. J. Shirar, O. L. Williams and B. C. Dian, *Chemical Physics Letters*, 2011, **508**, 10–16.

[6] M. Suzuki and K. Kozima, *Journal of Molecular Spectroscopy*, 1971, **38**, 314–321.

[7] H. Kim, R. Keller and W. D. Gwinn, *The Journal of Chemical Physics*, 1962, **37**, 2748–2750.

[8] E. Willemot, D. Dangoisse, N. Monnanteuil and J. Bellet, *Journal of Physical and Chemical Reference Data*, 1980, **9**, 59–160.

[9] R. W. Davis, A. Robiette, M. Gerry, E. Bjarnov and G. Winnewisser, *Journal of Molecular Spectroscopy*, 1980, **81**, 93–109.

[10] R. Bocquet, J. Demaison, L. Poteau, M. Liedtke, S. Belov, K. Yamada, G. Winnewisser, C. Gerke, J. Gripp and T. Köhler, *Journal of Molecular Spectroscopy*, 1996, **177**, 154–159.

[11] G. K. Drayna, *Ph.D. thesis*, Harvard University, 2016.

[12] P. L. Houston, *Chemical kinetics and reaction dynamics*, Courier Corporation, 2012.

[13] D. Patterson and J. M. Doyle, *Molecular Physics*, 2012, **110**, 1757–1766.