Supporting information for

Photochemistry of the Indoor Air Pollutant Acetone on Degussa P25 TiO_2 Studied by Chemical Ionization Mass Spectrometry

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UV-Vis Transmission of Catalyst Coatings

Representative samples of 1, 2, 5 and 10 layers of TiO_2 on quartz slides (ChemGlass) were made to determine the extent of UV light transmission through catalyst coatings used in this work. The UV transmission spectrum through each sample was recorded with an Ocean Optics USB2000 miniature fiber optic spectrometer. While the transmission of 254 and 365 nm light drops precipitously as the catalyst layer thickens (Figure 1 in manuscript), the transmission remains non-zero (~6%) even for the thickest samples examined (10 layers). Fitting parameters for exponential fits to the transmission data, which follows the form $C+Ae^{-Bl}$, where l is the number of TiO_2 layers, are presented in Table SI.1. This data indicates that under the experimental conditions used in this work, UV light is expected to be transmitted through the catalyst coating, providing a UV flux to the entirety of the sample. A spectrum taken interior of a quartz insert coated with 10 layers of TiO_2 verifies that UV radiation at 254 and 365 nm is transmitted through the quartz flow tube, quartz insert, and catalyst coating. This indicates that the expected active surface, the interior diameter of the coated flow tube insert, will be exposed to activating UV radiation under experimental conditions.

Analyte Characterization

NMR spectra were taken of liquid mesityl oxide and diacetone alcohol in deuterated chloroform using a high resolution, high sensitivity Varian INOVA-500 MHz spectrometer. For each sample, spectra were taken of the as-received compound and of an acetone-spiked sample. The spectrum of the as-received mesityl oxide in $CDCl_3$ display non-solvent singlet peaks at 6.092 ppm, 2.167 ppm, 2.140 ppm, and 1.886 ppm. Integration of these peaks is found to be 9.12, 36.34, 30.81, and 32.85, respectively. Spiking this sample with acetone results in an additional peak, producing a spectrum of five singlet peaks at 6.090 ppm, 2.174 ppm, 2.164 ppm, 2.137 ppm, and 1.884, with integrations of 5.47, 42.34, 17.96, 20.77, and 18.93, respectively. This data is summarized, with spectral assignment, in Table SI.2.

The spectrum of the as-received diacetone alcohol in $CDCl_3$ displays four non-solvent singlet peaks at 3.779 ppm, 2.623 ppm, 2.167 ppm, and 1.242 ppm. Integration of these peaks is found to be 0.27, 0.82, 1.08, and 2.83, respectively. Spiking this sample with acetone results in an additional peak, producing a spectrum of five singlet peaks at 3.781 ppm, 2.626 ppm, 2.170 ppm, 2.164 ppm, and 1.245. The two singlet peaks at 2.170 ppm and 2.164 ppm partially overlap (i.e. are not baseline resolved), and are therefore best included in a single integration. The four integrable peaks have integrations of 0.28, 0.80, 1.52, and 2.82, respectively. An analysis to separate the two peaks near 2.17 ppm for integration implies a 2:1 ratio for the two peaks, with the downfield peak having approximately twice the intensity of the upfield peak. This data is summarized, with spectral assignments, in Table SI.2.

Acetone in $CDCl_3$ is expected to result in a singlet peak at 2.17 ppm,[1] which is not observed in the as-received mesityl oxide or diacetone alcohol spectra, but appears in the spiked samples at 2.174 ppm for mesityl oxide and 2.170 ppm for diacetone alcohol. The lack of an acetone signature in the un-spiked NMR spectra implies that, on the order of the sensitivity of the technique (~2%) the mesityl oxide and diacetone alcohol from which gas phase samples are produced are pure.

To verify the purity of the gas phase samples themselves, FTIR spectra were taken using a Bio-Rad Excalibur FTS-3000 infrared spectrometer equipped with an MCT detector. Gas samples taken from previously prepared sample bulbs were allowed to fill a custom infrared cell. FTIR spectra of these two species are somewhat less straightforward to interpret than the NMR data due to the overlap or near overlap of spectral features for vibrational modes found in related molecules such as acetone and mesityl oxide. Nevertheless, the resulting spectra provide indications that the gas samples are pure (Figure SI.1).

For the mesityl oxide sample, spectral features at 963 cm^{-1} (R_2C=CH-),[2,3] 1218 cm^{-1} (C-C),[2] 1366 cm^{-1} (CH_3 bending modes),[4] 1448 cm^{-1} (CH_2 bending modes),[3,5] 1635 cm^{-1} (C=C aliphatic),[3,5] 1708 cm^{-1} (C=O),[2] and 2930 $cm^{-1}$and 2983 cm^{-1} (CH_2 stretching modes),[2,4] are consistent with those expected for mesityl oxide, either in the gas phase or on a surface. More importantly, these peaks are generally distinguishable from those expected for the same functional groups in acetone,[6] as shown in Figure SI.1a and SI.1b. Similarly, the spectrum for diacetone alcohol displays signatures for the expected vibrational modes: 1219 cm^{-1} (C-C),[2] 1325 cm^{-1} (R_3C-OH),[2] 1377 cm^{-1} (CH_3 bending modes),[4] 1457 cm^{-1} (CH_2 bending modes),[3,5] 1726 cm^{-1} (C=O),[2] 2930 cm^{-1} and 2986 cm^{-1} (CH_2 stretching modes),[2-4] and 3563 cm^{-1} (free OH).[2,3] Again, these peaks appear to be more consistent with a reference spectrum for diacetone alcohol[6] than with an acetone reference (Figure SI.1c and SI.1d). These FTIR spectra, taken together with the NMR data discussed above, indicate that the samples of mesityl oxide and diacetone alcohol used in these studies are sufficiently pure to assume that the CIMS peaks seen at positions other than the parent peak are not due to simple volatilization of impurities contained in the original sample bulbs, but rather result from either fragmentation or surface reaction/photochemistry.

CIMS Peak Identification

While it is possible that the signal at ~45 amu in the CIMS data presented above stems from proton transfer to acetaldehyde, Coronado et al. found in DRIFTS studies of acetone adsorbing to TiO_2 that this species is not detected in the gas phase[7] but exists only as a surface-bound intermediate. In Coronado's work, surface acetaldehyde was easily quantifiable, so although the absorption cross section for acetaldehyde is smaller than that for CO_2 (maximum cross sections[8] of 4×10^{-19} cm^2 $molec^{-1}$ for the acetaldehyde carbonyl stretch near 1750 cm^{-1} versus 1.2×10^{-17} cm^2 $molec^{-1}$ for the CO_2 antisymmetric stretch near 2300 cm^{-1}),[9] gas phase acetaldehyde should be identifiable if it is formed in the surface reaction. Since a process similar to that observed by Coronado et al. likely occurs in our experiments, it is expected that the signal we observe arises from the formation of carbon dioxide.

To confirm the assignment of the peak at ~45 amu as carbon dioxide, spectra were taken of pure acetaldehyde (near 2×10^{-6} Torr) and pure CO_2 (taken by capturing the gas as it sublimed from dry ice, producing a partial pressure near 2×10^{-2} Torr) were obtained (Figure SI.2). CO_2 can be identified in CIMS spectra as both a proton transfer product just above 45 amu, and as a charge transfer product, detected just above 44 amu. In contrast, pure acetaldehyde is seen only as the proton transfer product at 45 amu. Although the signal levels during photooxidation in our experiments are low, it can be seen in Figure 6b that there are two peaks in all but the diacetone alcohol system. For diacetone alcohol, low signal levels make it difficult to see either peak clearly in the mass trace, though the signal change is clear in the CIMS versus time traces presented. The existence of both the charge transfer and proton transfer peaks in Figure 6b indicates that the product detected at 45 amu in these experiments is primarily CO_2. However, without separate spectroscopic measurements such as *in situ* FTIR to confirm this, contributions to this peak from both carbon dioxide and acetaldehyde cannot be categorically ruled out. Both acetaldehyde and CO_2 represent photocatalytic products of acetone, however, and the peak at 45 amu can therefore be used as a marker for photooxidation processes.

References:

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Table SI.1: Fitting parameters for exponential fits to the transmission data for UV light through TiO_2 on quartz.

Wavelength	**A [%]**	**B [l^{-1}]**	**C [%]**
254 nm	80 ± 10	0.6 ± 0.2	9 ± 7
365 nm	80 ± 10	0.5 ± 0.2	11 ± 8

Table SI.2: NMR spectral data and assignments for two mesityl oxide samples and two diacetone alcohol samples, with assignments based on references 1 and 6.

Sample	Position [ppm]	Integration (Relative)	Assignment
Mesityl oxide: As received	6.092	9.12 (1)	Vinylic H
	2.167	36.34 (3.98)	α-CH_3
	2.140	30.81 (3.38)	E-β-CH_3
	1.886	32.85 (3.60)	Z-β-CH_3
Mesityl oxide: Acetone-spiked	6.090	5.47 (1)	Vinylic H
	2.174	42.34 (7.74)	Acetone CH_3
	2.164	17.96 (3.28)	α-CH_3
	2.137	20.77 (3.80)	E-β-CH_3
	1.884	18.93 (3.46)	Z-β-CH_3
Diacetone alcohol: As received	3.779	0.27 (1)	Alcohol H
	2.623	0.82 (3.04)	α-CH_2
	2.167	1.08 (4)	α-CH_3
	1.242	2.83 (10.5)	β-CH_3
Diacetone alcohol: Acetone-spiked	3.781	0.28 (1)	Alcohol H
	2.626	0.80 (2.86)	α-CH_2
	2.170	0.95 (3.39)	Acetone CH_3
	2.164	0.43 (1.54)	α-CH_3
	1.245	2.82 (10.1)	β-CH_3

Table SI.3: Uptake coefficients for acetone, formic acid, acetic acid, mesityl oxide, and diacetone alcohol, measured using CIMS versus time traces, at a temperature of 298K.

Analyte	Average Partial Pressure [Torr]	Average Uptake Coefficient [--]
Acetone	1.21×10^{-6}	3.1×10^{-4}
	6.27×10^{-6}	3.3×10^{-4}
Formic acid	1.44×10^{-6}	1.6×10^{-4}
	6.18×10^{-6}	7.3×10^{-5}
Acetic acid	1.38×10^{-6}	1.8×10^{-4}
	6.22×10^{-6}	8.4×10^{-5}
Mesityl oxide	1.37×10^{-6}	1.5×10^{-4}
	6.12×10^{-6}	3.9×10^{-4}
*Diacetone alcohol	1.21×10^{-6}	8.4×10^{-4} (59 amu)
		2.3×10^{-3} (99 amu)
	6.40×10^{-6}	6.2×10^{-4} (59 amu)
		2.0×10^{-3} (99 amu)

* For diacetone alcohol samples, the uptake coefficient was measured for both the mass spectral signature at ~59 amu (Ace) and that at ~99 amu (MO). See text for details.

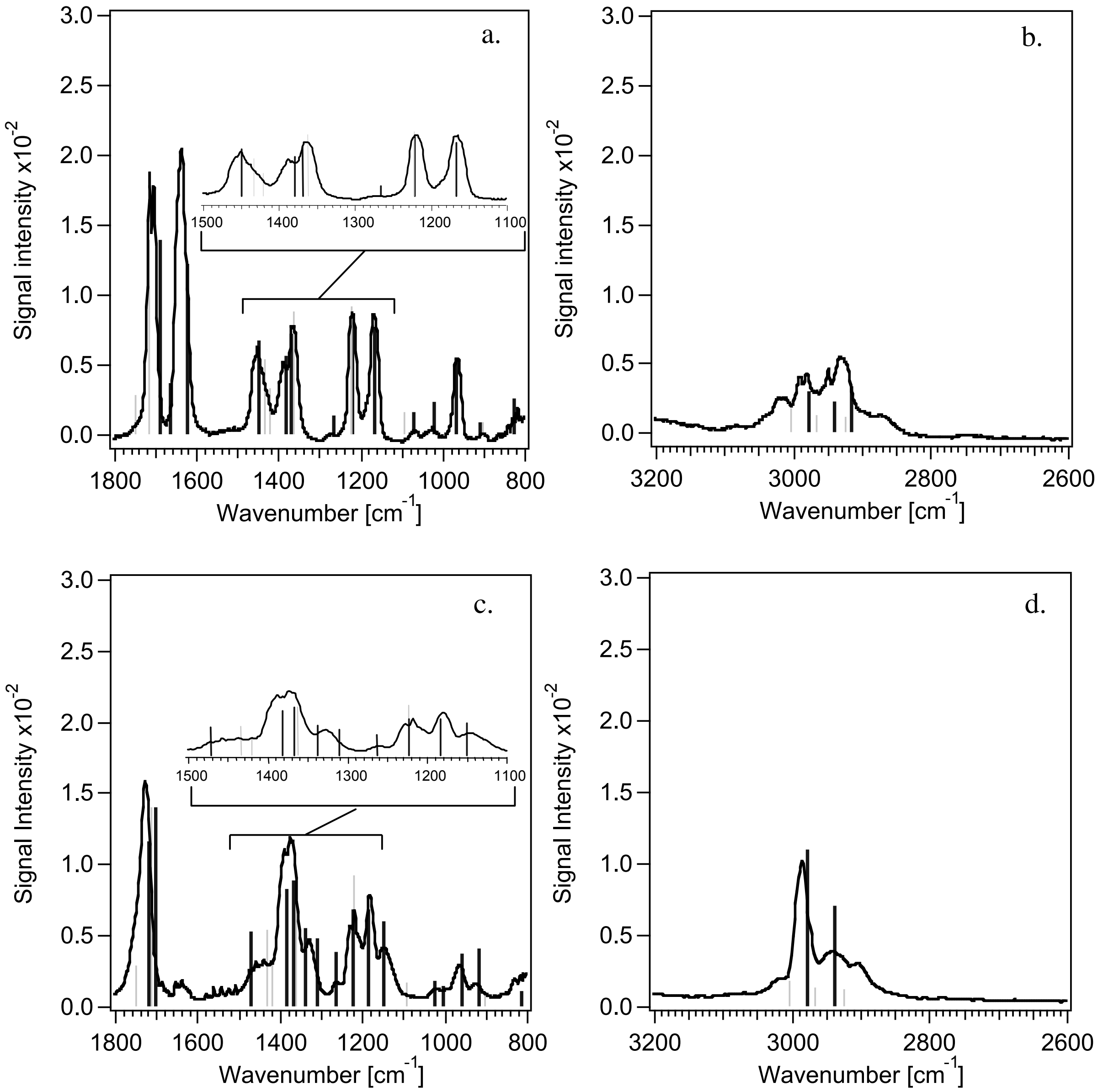

Figure SI.1: Gas phase FTIR spectra for: mesityl oxide (panels a and b) taken at 2 cm^{-1} resolution with 20 scans averaged, and diacetone alcohol (panels c and d) taken at 4 cm^{-1} resolution and with 60 scans averaged. Reference peak positions associated with acetone are marked with vertical light gray lines, while peaks associated with the pure analyte are marked with dark gray vertical lines. Reference spectra are from reference [6].

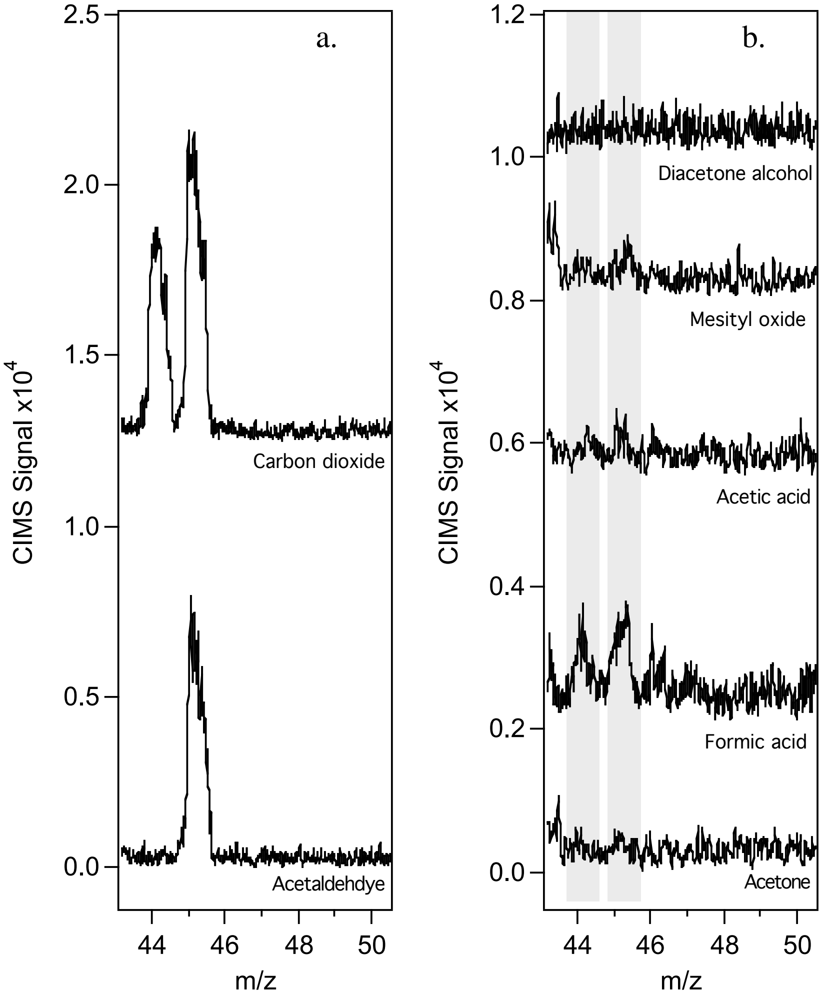

Figure SI.2: (a) Comparison of acetaldehyde and CO_2 CIMS spectra, and (b) CIMS spectra of each analyte studied in this work during CO_2 production.