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# Sunlight-driven combustion of HCHO in the troposphere: Photophysical Oxidation of HCHO produces HO<sub>2</sub> radicals

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## Abstract

Formaldehyde, HCHO, is the highest volume carbonyl in the atmosphere. After absorption of sunlight at wavelengths shorter than 330 nm it dissociates to form H and HCO radicals, which react with O<sub>2</sub> to form HO<sub>2</sub>. In this paper, we report direct experimental detection of HO<sub>2</sub> radicals  
5 by cavity ringdown spectroscopy following photolysis of HCHO at photon energies *below* the energetic threshold for radical formation. At these same photon energies, end-product analysis by Fourier-transform infrared spectroscopy reveals indirectly the formation of HO<sub>2</sub> at 1 Bar pressure through the detection of formic acid, a product from secondary HO<sub>2</sub> reactions with the parent HCHO. Supported by electronic structure theory and master equation calculations, we attribute  
10 this to *photophysical oxidation* (PPO): photo-excited HCHO relaxes non-radiatively to the ground electronic state where the vibrationally activated molecules react with O<sub>2</sub>. Thus PPO occurs under far-from-equilibrium conditions: the HCHO vibrational energy is close to the absorbed photon energy, whereas other degrees of freedom are thermalised. Radical formation via PPO has the opposite pressure dependence to photolysis – increasing for higher pressure of O<sub>2</sub>. PPO is likely to  
15 be a general mechanism in tropospheric chemistry.

## Introduction

Sunlight drives the chemistry of the atmosphere. Near the Earth's surface, absorption of light by molecules such as carbonyls produces highly reactive radical species. These radicals rapidly react with atmospheric oxygen in what is commonly described as photochemical oxidation (PCO), *i.e.* photolysis followed by oxidation. The resulting atmospheric HO<sub>2</sub> and OH radicals then initiate further radical chain reactions that cleanse the atmosphere of most pollutants and oxidise atmospheric carbon to CO<sub>2</sub> (1,2).

In the atmosphere, a gas phase molecule has four principal fates. It can *i)* absorb light and photolyse, or *ii)* react with a highly reactive species such as OH, NO<sub>3</sub> or O<sub>3</sub>, or *iii)* undergo wet or dry deposition, or *iv)* the molecule might be long-lived, and hence globally distributed throughout the atmosphere. In this paper, we propose that *i)* and *ii)* combine in a new process where photo-activated molecules formed after a radiationless transition (a photophysical process) react with O<sub>2</sub> in a reaction that is similar to combustion, but under far-from-equilibrium conditions.

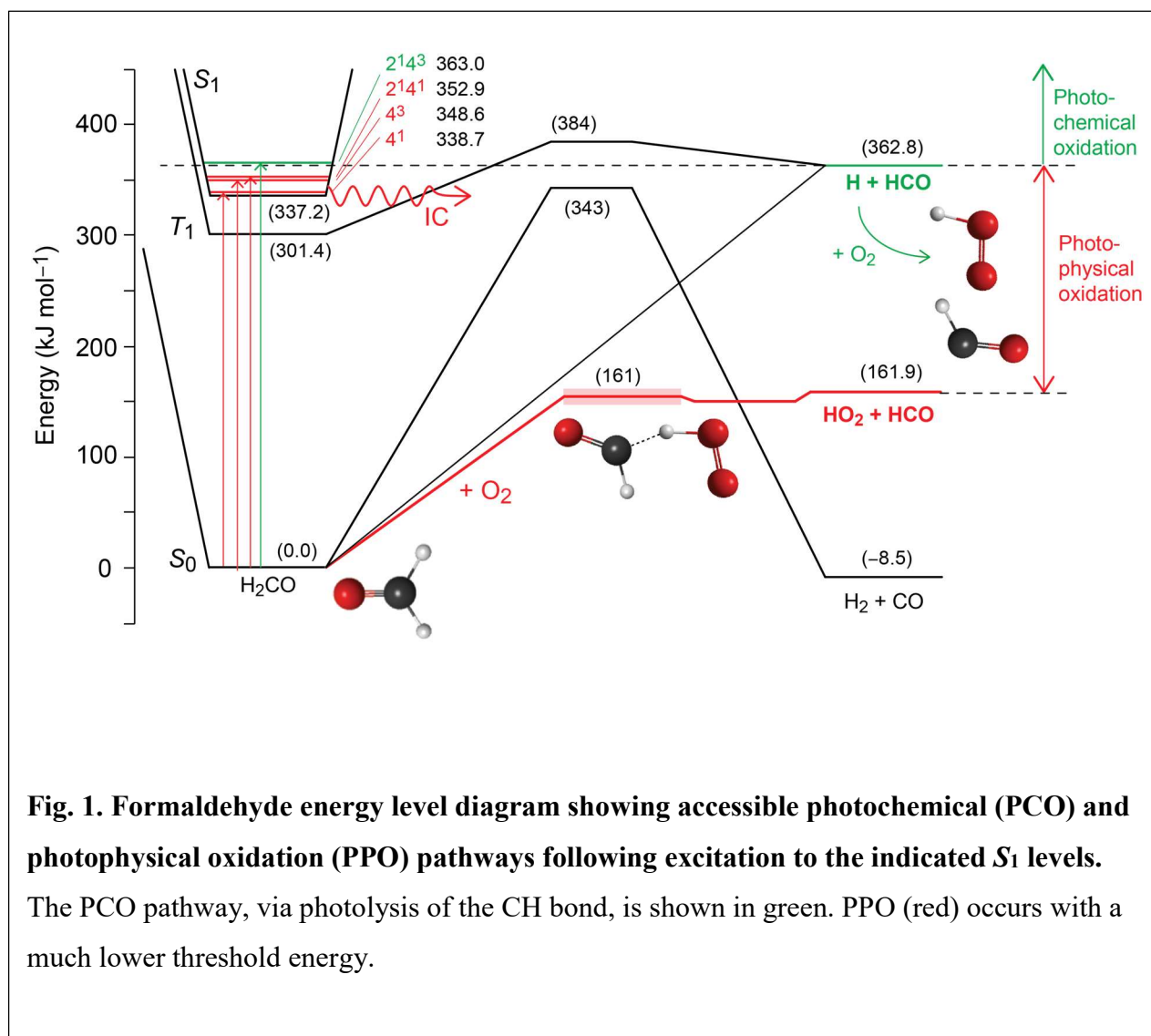
The reaction of activated (internally-excited) molecules is well-known. The products of exothermic reactions can be formed with an inverted distribution of energy in internal vibrational states. These chemically-activated molecules may react faster than those at thermal energies. For example, in an atmospheric context, Glowacki *et al* have shown that the chemically-activated hydroxyvinyl radical (HC=CHOH), formed from the reaction of OH with ethyne (HCCH), undergoes a different atmospheric fate depending on the degree of internal activation (3).

Vibrational activation can also be achieved by infrared (IR) overtone excitation as discussed in an atmospheric context by Vaida and Donaldson (4). Such IR-induced activation in molecules such as H<sub>2</sub>SO<sub>4</sub> can explain the SO<sub>2</sub> vertical profiles in the polar stratosphere. The enhanced reaction of electronically-activated species in the atmosphere is also well-known. Oxygen atoms in their excited <sup>1</sup>D electronic state react facily with important atmospheric molecules, such as H<sub>2</sub>O and N<sub>2</sub>O, whereas ground state O(<sup>3</sup>P) atoms are unreactive (5).

In this paper we demonstrate a different type of activated chemistry in formaldehyde (HCHO), and show that it is relevant under tropospheric conditions. The process is shown in Figure 1. A UV photon excites HCHO to its first excited singlet state, S<sub>1</sub>. Internal conversion (IC) transfers the energy to the ground electronic state, S<sub>0</sub>. As a photophysical process, energy is conserved and the energy of the excited electronic state is transferred to vibrational energy in the ground electronic

state. The photophysically-activated molecule then reacts with O<sub>2</sub> to initiate photophysical oxidation (PPO), forming HCO and HO<sub>2</sub> radicals. In the case of HCHO, the critical threshold energy for PPO (161 kJ mol<sup>-1</sup>, (6)) is less than half of that required for PCO via radical formation from direct photolysis of the C-H bond (362.8 kJ mol<sup>-1</sup>).

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Like other activated chemical processes, PPO is a *far-from-thermal-equilibrium* mechanism. The reactive degrees of freedom in HCHO (vibration, rotation and translation) are not in equilibrium with each other, nor with the background gas. Consequently, PPO reactions will not behave with a conventional temperature and pressure dependence. Indeed, we predict PPO reactions in the troposphere will produce different chemical products, and have a reverse pressure dependence to conventional PCO, resulting in, as yet, unknown effects on tropospheric cycles. We predict PPO is a general mechanism for molecules that absorb light and conclude this paper by considering the implications that PPO might have for chemical models of the troposphere.

Formaldehyde (HCHO) is the simplest carbonyl and one of the most important organic species in the atmosphere. It is both directly emitted, and formed as an oxidation product of volatile organic species. Formaldehyde absorbs light in the near-ultraviolet spectrum ( $\lambda \gtrsim 300$  nm at the Earth's surface), initiating several well-characterised photochemical processes (7-13). As a small molecule, HCHO is also a benchmark for high-level *ab initio* theory (14-17). The depth of knowledge about HCHO photochemistry – in the laboratory, in the atmosphere and theoretically – makes it an ideal candidate to demonstrate, unequivocally, the presence of the PPO reaction.

The spectroscopy, photochemistry and energetics of HCHO, applicable to this work, are described in detail in the supplementary information. Figure 1 shows a schematic of the relevant electronic states, energy levels and chemical pathways following near-UV excitation. When excited above the radical threshold ( $\lambda < 330$  nm), HCHO has two photolysis outcomes:



with threshold energies shown in Fig. 1. The total HCHO photolysis quantum yield (QY),  $\phi_{\text{ph}}$ , for  $\lambda < 330$  nm is essentially unity and largely pressure independent (18-25). In the troposphere, the radical products from R1 react quickly with O<sub>2</sub> to produce HO<sub>2</sub>:



where M is a collision partner needed to stabilise HO<sub>2</sub>. The three reactions, R1, R3 and R4, together with the reaction of HCHO with OH and Cl atoms, constitute the main oxidation

pathways of HCHO (26). The conventional PCO of HCHO, R1 followed by R3 and R4, can only occur at absolute energies above the R1 radical threshold, which is known accurately to be 362.80 kJ mol<sup>-1</sup> (27). Photon energies lower than this threshold can cause PCO if thermally excited HCHO molecules absorb light. Care is taken in this work not to excite vibrational hot-bands (see  
5 below).

At lower excitation energy (corresponding to longer wavelengths,  $\lambda > 330$  nm), only the molecular photolysis channel, R2, is possible, and tunnelling allows R2 to proceed at energies below the classical energetic threshold shown in Fig. 1. Under tropospheric conditions,  $\phi_{ph}$  is less than unity and pressure dependent (18-22); there is competition between R2 and collisions with (mainly) N<sub>2</sub> and O<sub>2</sub>, which remove excess vibrational energy and return HCHO to thermal equilibrium. Here,  
10 we demonstrate that these collisions with O<sub>2</sub> can also lead to PPO of HCHO:



15 where the double dagger represents vibrationally-activated HCHO.

## Results

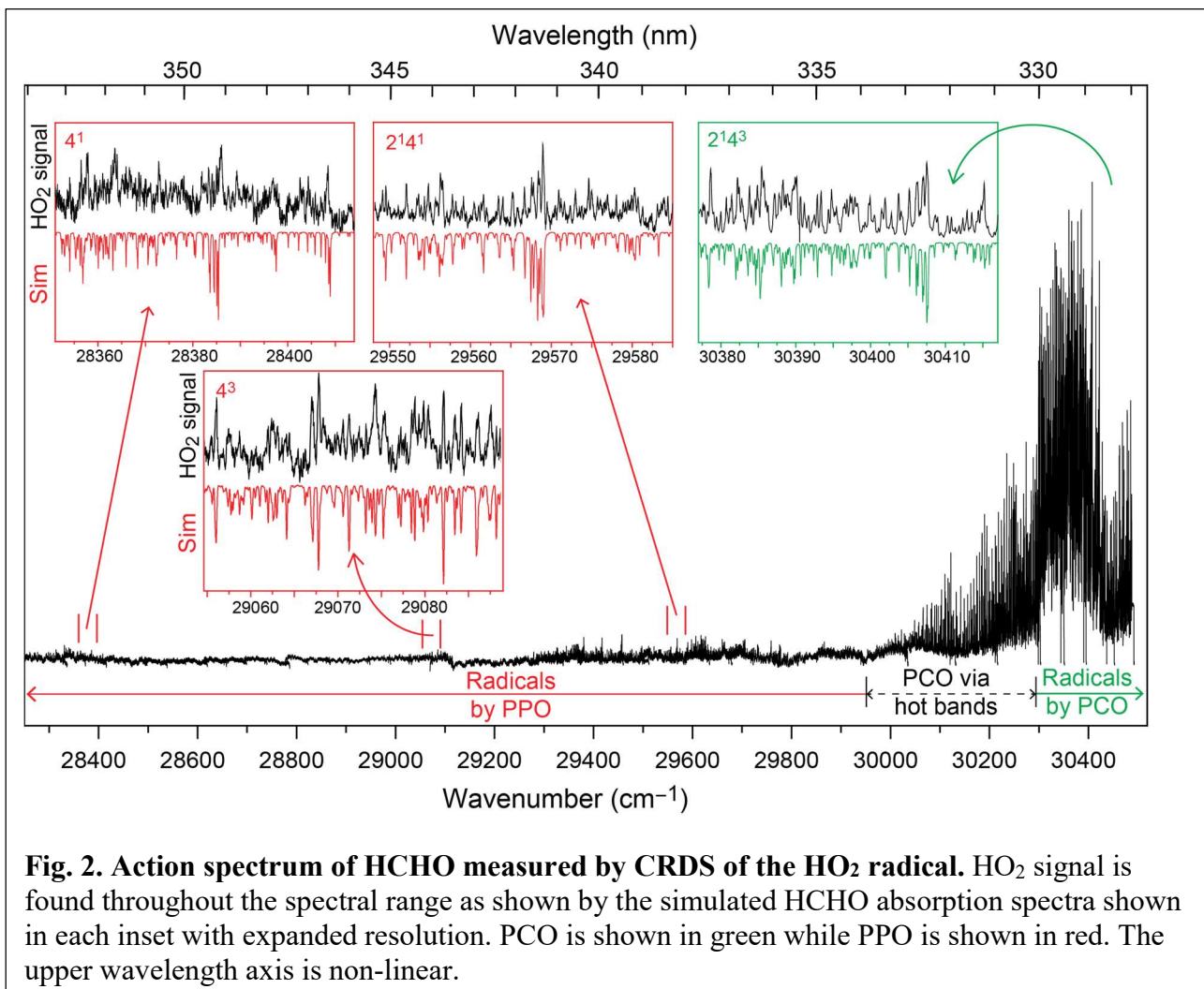
We employed two experimental techniques, with interpretation supported by *ab initio* electronic structure theory calculations of the critical energies of R5 and Master Equation kinetic modelling  
20 of PPO under experimental conditions. In both experiments, a laser was used to excite specific vibrational levels of the *S*<sub>1</sub> electronic state of HCHO as indicated in Fig. 1. Laser excitation, coupled with the well-known spectroscopy of HCHO (see Supplementary Information, SI), ensure that the initial, photoexcited energy of HCHO is very well-defined. The lower-lying excited levels, 4<sup>1</sup>, 4<sup>3</sup> and 2<sup>1</sup>4<sup>1</sup> lie 24, 14 and 10 kJ/mol below the radical threshold, respectively, while the higher  
25 lying level, 2<sup>1</sup>4<sup>3</sup>, is 0.2 kJ mol<sup>-1</sup> above the radical threshold. The 4<sup>1</sup> level lies below the R2 energetic barrier to molecular products, however tunnelling through the barrier is efficient at this energy and molecular products are still observed, even in the presence of collisions at 1 Bar pressure (11, 21).

In the first experiment, cavity ring down spectroscopy (CRDS) was used in a low-pressure flow  
30 cell to measure *in situ* production of HO<sub>2</sub>, following HCHO irradiation in the presence of O<sub>2</sub>. In

the second experiment, Fourier-transform infrared (FTIR) spectroscopy was used to measure end-products following irradiation of HCHO in a static cell as a function of pressure. The CRDS experiments demonstrate unequivocal production of HO<sub>2</sub> radicals, but at a maximum pressure of 50 Torr. The FTIR experiments implicitly demonstrate PPO is operative at 1 Bar pressure.

5 Further experimental details are provided in References 28 and 29 and in the Methods section (see SI).

*Direct CRDS detection of HO<sub>2</sub>*: Figure 2 shows a CRDS action spectrum, where HO<sub>2</sub> absorption is plotted as a continuous function of photolysis wavelength. The complexities in the spectrum arise from the vibration-rotation structure of the HCHO electronic spectrum, which is well known (30, 31). The spectrum can be simulated and assigned, as shown in the higher resolution inset panels. Above the radical threshold, transitions are very intense due to efficient PCO production of HO<sub>2</sub> via R3 and R4. The inset panels also have clearly assigned HCHO structure, shown in red, where



**Fig. 2. Action spectrum of HCHO measured by CRDS of the HO<sub>2</sub> radical.** HO<sub>2</sub> signal is found throughout the spectral range as shown by the simulated HCHO absorption spectra shown in each inset with expanded resolution. PCO is shown in green while PPO is shown in red. The upper wavelength axis is non-linear.

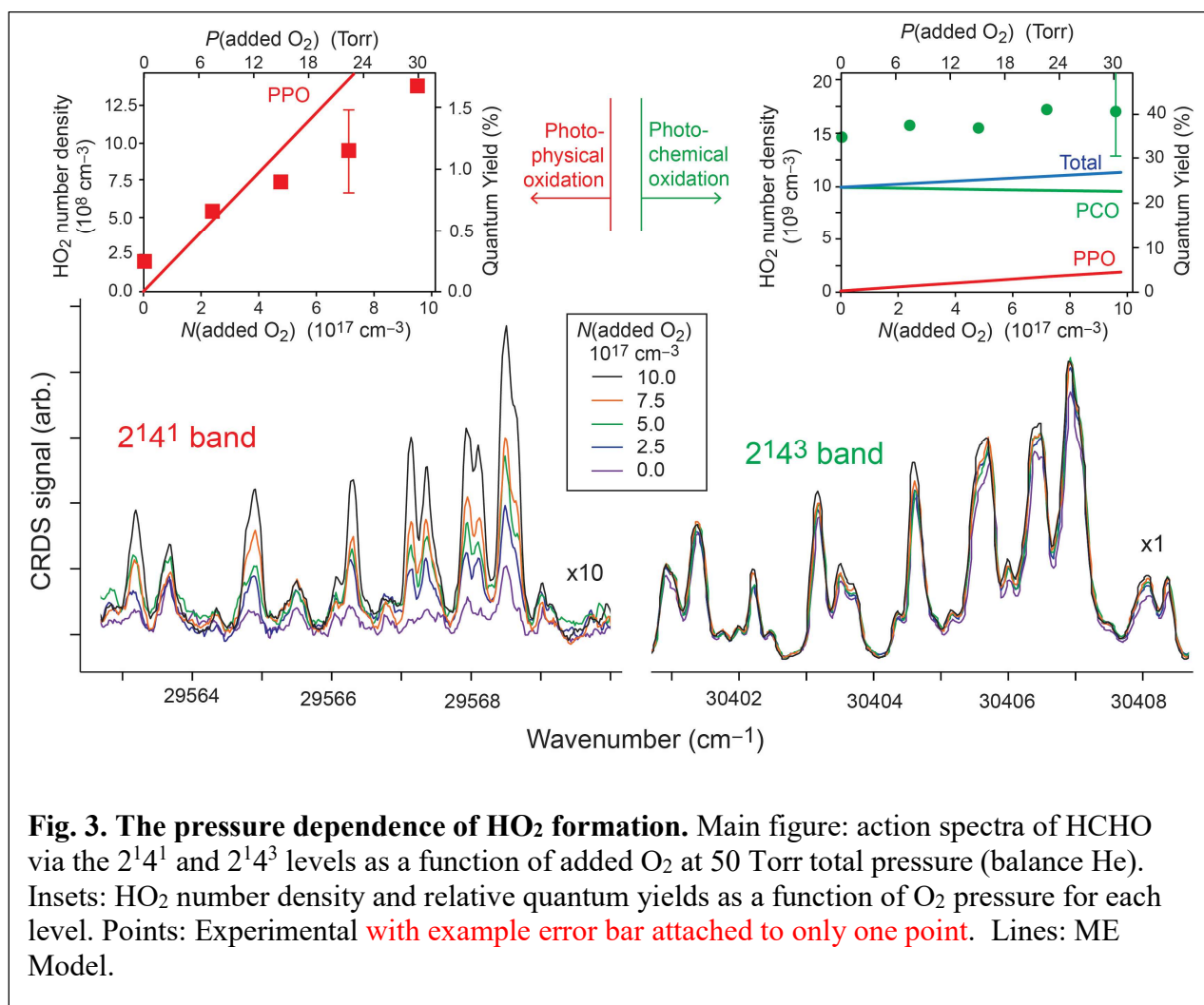
PCO production of HO<sub>2</sub> is not energetically possible. This is the region of photophysical production of HO<sub>2</sub>. The signal-to-noise ratio for excitation to the 4<sup>3</sup> and, especially, 4<sup>1</sup> levels is



lower than  $2^1_4^1$  in the PPO region because the absorption strength of these bands is  $\sim 1/3$  that of  $2^1_4^1$ , and the laser energy is lower near  $4^1$ . As shown below, the PPO quantum yield, however, is similar.

The dependence of the HO<sub>2</sub> signal on O<sub>2</sub> pressure at a total pressure of 50 Torr (balance helium) is shown in Fig. 3. The HO<sub>2</sub> signal below the radical threshold ( $2^1_4^1$ ) shows a strong, linear increase with  $P(\text{added O}_2)$ . The continued observation of radicals, and their linear increase with O<sub>2</sub> pressure are key observations of this work and indicate a new bimolecular chemical mechanism for radical formation.

The HO<sub>2</sub> signal above the radical threshold ( $2^1_4^3$ ) shows a small increase with increasing O<sub>2</sub> pressure. The observed HO<sub>2</sub> at  $P(\text{added O}_2) = 0$  is due to background O<sub>2</sub>, which we estimate from the measured leak rate as  $\sim 10^{14} \text{ cm}^{-3}$  (3 mTorr). Because the background O<sub>2</sub> is about four orders



of magnitude larger than the radical density, all reaction conditions are pseudo first-order and any H and HCO radicals formed from R1 should quantitatively form HO<sub>2</sub> via R3 and R4, that is, via

the conventional PCO mechanism. The slight increase in HO<sub>2</sub> as  $P(\text{added O}_2)$  is increased may be due to the presence of the PPO channel (R5) and/or reduced diffusion of H-atoms and HO<sub>2</sub> to the reactor walls and this is tested below.

5 End-product analysis using FTIR spectroscopy: Figure 4 shows FTIR product spectra, following 5 min irradiation of 1.0 Torr neat HCHO at 338.39 nm ( $2^1 4^1$ , below the photochemical threshold for radical formation), as well as diluted in 160 Torr N<sub>2</sub>, 160 Torr O<sub>2</sub> and 760 Torr synthetic air (79% N<sub>2</sub>, 21% O<sub>2</sub>). The parent HCHO spectrum has been subtracted, revealing only features of photolysis products. The asterisks show where a residual, sharp HCOH Q-branch feature has been  
10 manually removed. The saturation of this Q-branch at low pressure causes a small non-linear pressure dependence and so is difficult to completely subtract. Similar spectra following excitation to the HCHO  $4^1$  (352.48 nm) and  $2^1 4^3$  (329.06 nm) levels in synthetic air are shown in Fig. S1. The FTIR spectra for neat HCHO photolysis, and in the presence of N<sub>2</sub>, show only CO, which is formed via R2 (the H<sub>2</sub> co-product does not absorb IR light). The FTIR product spectra taken in the  
15 presence of O<sub>2</sub> show an additional product: formic acid, HCOOH. The presence of HCOOH can be explained via the known reaction scheme (26, 32, 33):

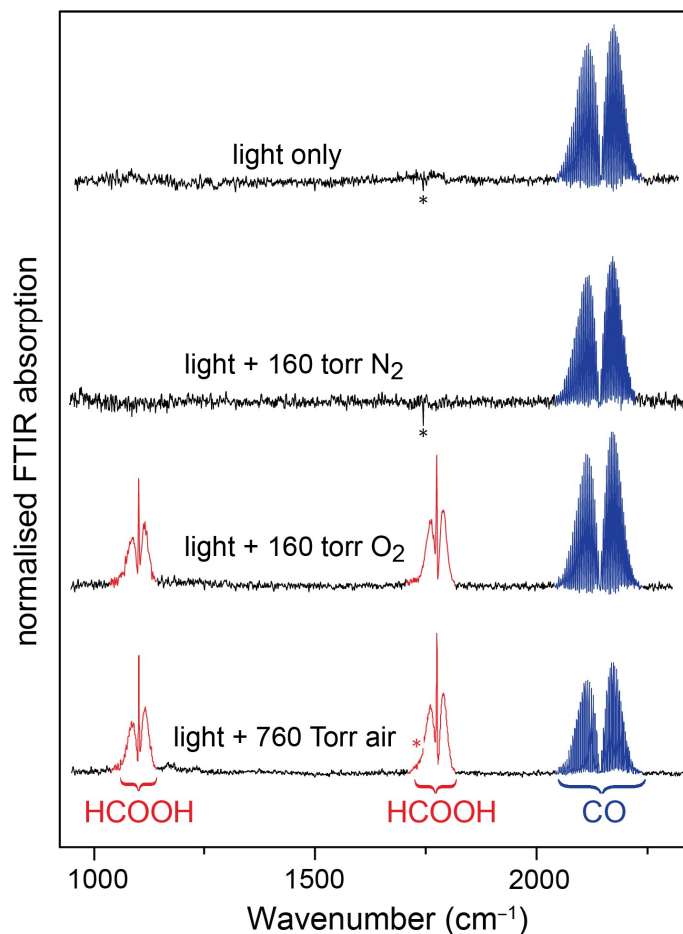


where M is a buffer gas, and HO<sub>2</sub> has been assumed, previously, to have formed via PCO. The double arrow indicates that a sequence of elementary reactions leading to HCOOH, and these are  
20 expanded in supplementary information (Fig. S2). The observation of HCOOH as an end-product, following excitation to the HCHO  $2^1 4^1$  and  $4^1$  levels in 760 Torr synthetic air (Figs 4 and S1, respectively), confirms production of HO<sub>2</sub>, at pressures relevant in the troposphere, at excitation energies below the HCHO radical threshold.

## 25 Discussion

Our experimental results present a convincing case that low energy photo-excitation of HCHO allows it to react with O<sub>2</sub>. The CRDS experiments demonstrate HO<sub>2</sub> is formed at energies up to 24 kJ mol<sup>-1</sup> below the radical threshold. The FTIR experiments at 1 Bar pressure of air show formation of HCOOH below the radical threshold, consistent with reaction between HO<sub>2</sub> and the

parent HCHO. The linear dependence of HO<sub>2</sub> with O<sub>2</sub> concentration seen in the CRDS experiments implies a bimolecular reaction between photo-excited HCHO and O<sub>2</sub>.



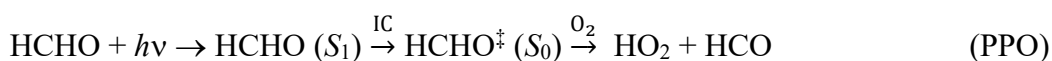
**Fig. 4: FTIR spectra of reaction end products following excitation of 1 Torr HCHO to the  $2^1_4^1$  level in different buffer gases as indicated.** Spectra are on the same scale but displaced vertically for presentation. HCOOH is only formed in the presence of O<sub>2</sub>. **The asterisks show where a sharp residual HCHO Q-branch feature remains even after subtraction of parent spectrum.**

- 5 The PPO mechanism: Three HCHO electronic states could be involved in reaction with O<sub>2</sub>: *i*) the initially prepared  $S_1$  state, *ii*) the  $T_1$  state, formed after intersystem crossing (ISC), or *iii*) highly vibrationally excited states of  $S_0$ , formed following internal conversion (IC) from  $S_1$ .

Reaction with HCHO ( $T_1$ ) is highly unlikely. HCHO is a small molecule in radiationless transition theory (34) – the density of states in its triplet manifold is very sparse at our experimental energies. Consequently, the ISC rate is strongly dependent on the initially excited HCHO rotation-vibration level. For the levels we consider, this manifests in highly variable fluorescence lifetimes, which vary by more than two orders of magnitude (35), and markedly different reaction dynamics, varying between  $T_1$ - and  $S_0$ -dominated reaction (9, 36). The HO<sub>2</sub> action spectrum in Fig. 2, however, shows an intensity pattern that is fit well for each vibrational level, at the level of individual rotational states, by a single simulated absorption spectrum. This implies a uniform (constant) relationship between the HCHO levels excited and the production of HO<sub>2</sub>, allowing us to discount HCHO ( $T_1$ ) as the reactive species. This conclusion is consistent with previous investigations of the photophysics of HCHO at these energies (37).

Reaction of O<sub>2</sub> with HCHO ( $S_1$ ) correlates with HCO in the electronically excited  $\tilde{A}(^2A')$  state. Although the HCO( $\tilde{A}$ ) + HO<sub>2</sub> products are energetically accessible, the  $\tilde{A}$  state of HCO is linear and this nuclear rearrangement will result in a significant energy barrier. We observe HO<sub>2</sub> and HCOOH following excitation of the lowest accessible HCHO ( $S_1$ ) state,  $4^1$ , with  $\nu_4' = 124.5 \text{ cm}^{-1}$  (30). In addition, the PPO QY (see below) is the same, within error, for the  $2^14^1$  and  $4^1$  states, even though the  $4^1$  state is  $\sim 1200 \text{ cm}^{-1}$  lower in energy. This suggests a critical energy for PPO that is far below the  $4^1$  state, rather than one with a significant barrier. Although we cannot definitively rule it out, HCHO ( $S_1$ ) reaction is unlikely because the reaction barrier is expected to be significantly higher than the available energy of the colliding molecules.

The remaining possibility is that reaction occurs between highly vibrationally excited,  $S_0$  HCHO (HCHO $^\ddagger$ ) and O<sub>2</sub>:



HCHO $^\ddagger$  has extremely high, non-thermal, vibrational energy arising from absorption of a photon but all other degrees of freedom, including the HCHO and O<sub>2</sub> translational and rotational energy, are thermalised at  $\sim 300 \text{ K}$ .

Theoretical validation of the PPO mechanism: There has been one previous theoretical study of R5 (38), which indicates a zero-point corrected barrier between 152 and 155 kJ/mol and a dipole-bound complex in the exit channel. We have re-examined the energetics of R5 using electronic structure theory. Details and discussion of these calculations are provided as supplementary

information. The lowest energy saddle point for R5 corresponds to an anti-periplanar orientation of the O<sub>2</sub> with respect to the C=O bond in HCHO. The threshold energy is sensitive to the level of electronic structure theory used and we calculate a range of 151.0 – 175.4 kJ mol<sup>-1</sup>, with a recommended zero-point corrected value of 161.4 kJ mol<sup>-1</sup>, both of which are shown in Fig. 1. At many levels of theory, the R5 saddle point is submerged, consistent with barrierless reverse reaction (39, 40).

The ‘late’ saddle point for R5 and the small energy difference between optimised anti-periplanar and syn-periplanar saddle points (Tables S2 and S3) suggest the potential energy surface in the vicinity of the saddle point is relatively flat with respect to O<sub>2</sub> in- and out-of-plane rotation, that is, O<sub>2</sub> can react with HCHO at almost any angle. Combined with our recommended threshold energy and the reaction enthalpy (6), this suggests PPO is energetically feasible and likely very efficient. Indeed R5 has been found to be efficient in shock tube experiments (39-43), although here all degrees of freedom, including relative translation and rotation, are in thermal equilibrium at elevated temperature.

PPO quantum yields: We determine  $\phi_{\text{PPO}}$  in CRDS experiments by internal calibration. Above the R1 threshold, photo-excitation results in two HO<sub>2</sub> radicals, via R3 and R4 with known QY,  $\phi_1 = 0.40 \pm 0.06$  at  $\lambda = 329 - 331$  nm. The radical QY is reported to be pressure-independent (24, 25). We do observe a weak pressure dependence for this channel, however the variation is within the uncertainty of the literature measurements and we use  $\phi_1 = 0.40 \pm 0.06$  as our internal calibration. The PPO reaction also produces two HO<sub>2</sub> radicals, via R5 and R4. We calculate  $\phi_{\text{PPO}}$  from the ratio of the observed HO<sub>2</sub> number density following excitation of the lower energy levels, compared to the 2<sup>1</sup>4<sup>3</sup> level. The HCHO absorption cross-section for each transition is known and corrected for, which then yields the wavelength-dependent QY,  $\phi_{\text{PPO}}$ . At 30 Torr added O<sub>2</sub>, we determine  $\phi_{\text{PPO}} = 0.017 \pm 0.005$  at 338 nm (2<sup>1</sup>4<sup>1</sup>),  $0.025 \pm 0.010$  at 343 nm (4<sup>3</sup>) and  $0.014 \pm 0.007$  at 352 nm (4<sup>1</sup>), where the uncertainty arises from the combined uncertainty of the fit to literature absorption spectra and the uncertainty in the literature QY of the 2<sup>1</sup>4<sup>3</sup> level. Details of these calculations are provided as SM.

Extraction of the PPO QY in FTIR experiments is challenging because the experiments measure the HCOOH end-product, whereas, as shown Fig. S2, HO<sub>2</sub> production following PCO and PPO is catalytic. Therefore measured HCOOH QYs do not reflect the primary QY for PCO or PPO.

### Master Equation modelling of HO<sub>2</sub> formation

A Master Equation (ME) model was developed, as described in SI, to simulate the CRDS experiments. The model includes IC of HCHO from  $S_1$  to  $S_0$  and collisional energy transfer within the  $S_0$  and  $S_1$  electronic states. The  $T_1$  state was not included. As discussed above, there is no  
5 evidence of the involvement of  $T_1$  and, further, IC is known to be the dominant non-radiative relaxation mechanism in HCHO (37). Reactions R1, R2 and R5 were used to calculate QYs for H + HCO, H<sub>2</sub> + CO and HCO + HO<sub>2</sub>.

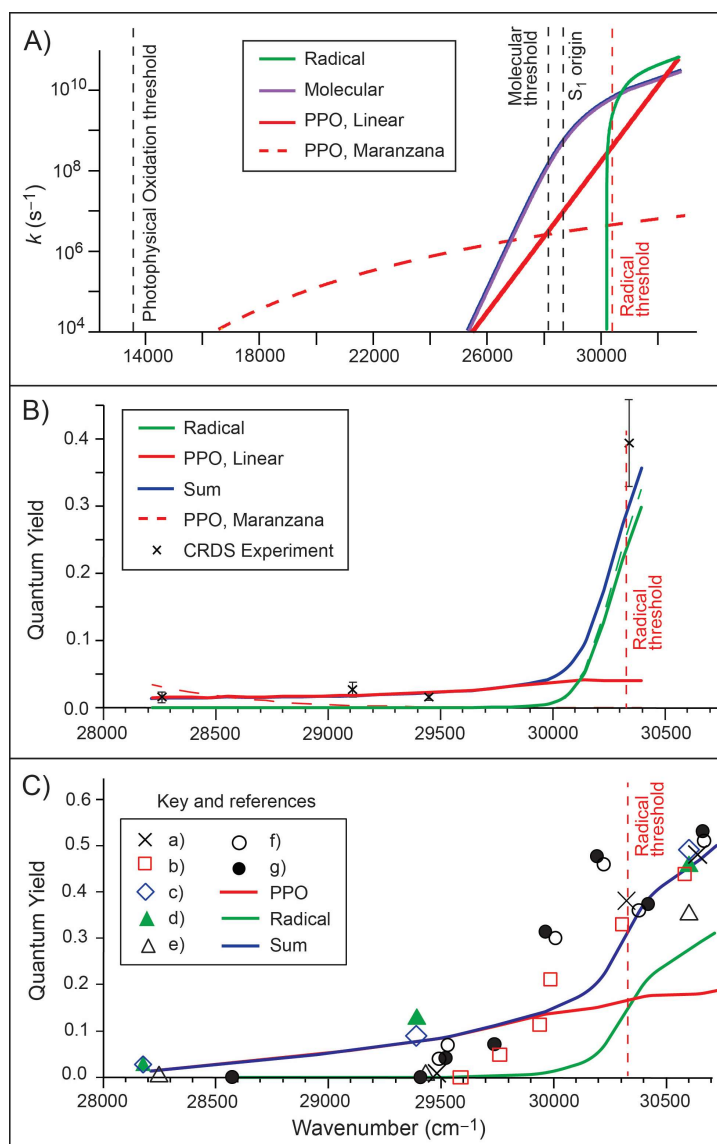
The IC rate coefficients were determined from the experimentally observed non-radiative lifetimes of the distinct HCHO  $S_1$  states (37). Microcanonical molecular channel rate coefficients for R2  
10 were taken as the  $J = 10$  rate coefficients, as calculated by Troe (11). These rate coefficients include anharmonic corrections and parabolic tunnelling, with a  $J = 0$  barrier height of 342.6 kJ mol<sup>-1</sup> (11, 44). As described in SI, Troe's expression for the R1 radical channel QY (11) was refit to the available experimental data and used to obtain a microcanonical rate coefficient for R1.

Two methods were used to model the PPO rate coefficient – a bottom-up approach calculating  
15  $k_{\text{PPO}}$  from first principles, and a top-down empirical approach fitting  $k_{\text{PPO}}$  to the experimental data using an assumed functional form. The bottom-up approach used the semi-microcanonical method of Maranzana *et al* (45). Here the internal energy distribution of the HCHO is microcanonical, corresponding to the laser excitation wavelength, and all other degrees of freedom are treated thermally. The empirical top-down method assumes  $k_{\text{PPO}}$  will be exponential with energy in the  
20 energy range considered with the intercept and exponent varied to minimise the least squares difference to experimental data obtained below the radical threshold.

The four different microcanonical rate coefficients considered are plotted as a function of internal (photolysis) energy in Fig. 5A.

Pressure-dependent reactant and product populations were modelled using a one-dimensional ME  
25 simulation in energy, as implemented in the Multiwell program package (46-48). A simple exponential energy transfer model was employed (11) together with Lennard-Jones collision frequencies for N<sub>2</sub> and O<sub>2</sub> at 300 K. The average downward collisional energy transfer is taken to be  $\langle \Delta E_{\text{down}} \rangle = 250 \text{ cm}^{-1}$  for collisions of  $S_0$  HCHO with N<sub>2</sub> and O<sub>2</sub> and  $\langle \Delta E_{\text{down}} \rangle = 25 \text{ cm}^{-1}$  for collisions of  $S_1$  HCHO with N<sub>2</sub> and O<sub>2</sub>, reflecting the sparse density of states in  $S_1$ . The ME  
30 simulations were run with 150,000 stochastic trials for 1.0  $\mu\text{s}$ , that is, for less than the duration

between laser pulses, with the final populations of each species being stable. More details of the ME modelling are provided as SI.



**Fig. 5: Energy dependence of rate coefficients and quantum yields.** A) First order, microscopic rate coefficients used in Master Equation calculations. The PPO rate coefficient is pseudo first order for 30 Torr O<sub>2</sub>. B) Quantum yields for various processes in CRDS experiments at 30 Torr added O<sub>2</sub>. C) Quantum yields at atmospheric pressure. a) Ref 18; b) Ref 19; c) Ref 20; d) Ref 21; e) Ref 22; f) Ref 23; g) Ref 24

Figure 5B shows ME results for the CRDS conditions at 30 Torr O<sub>2</sub>, 20 Torr He. The Maranzana form (45) of the PPO rate coefficient yields  $\phi_{\text{PPO}}$  that is close to experiment at the lowest 4<sup>1</sup> level.

5 However  $\phi_{\text{PPO}}$  drops with increasing energy and is essentially zero for the other two experimental energies. At higher energies, as seen in Fig. 5A, the R2 molecular channel rate coefficient rises

more steeply with energy in this region and out-competes the Maranzana  $k_{\text{PPO}}$ . This is not in accord with the experimental findings.

The energy-dependent HO<sub>2</sub> QYs obtained with  $k_{\text{PPO}}$  fit to the experimental data, solid red line in Fig. 5B, are within error of the CRDS experimental data below the radical threshold. When PPO is added to the radical channel QY, the overall radical yield is also in acceptable agreement with experiment at the 2<sup>1</sup>4<sup>3</sup> energy.

The ME simulations have also been used to predict the O<sub>2</sub> pressure dependence of the HO<sub>2</sub> QY (Fig. 3 and Table S8). The observed CRDS pressure dependence is modelled well, using the fitted  $k_{\text{PPO}}$ , with the strong linear increase in HO<sub>2</sub> QY with pressure reproduced for states below the radical threshold. The ME simulations also predict a much weaker linear increase in HO<sub>2</sub> QY with pressure for the 2<sup>1</sup>4<sup>3</sup> state, where PCO via the radical channel products dominates HO<sub>2</sub> production. Indeed the ME simulations predict, with increasing pressure, a slight quenching of the PCO QY and an enhancement of PPO.

Energy dependent QYs from ME simulations at 1 Bar pressure, using the fitted  $k_{\text{PPO}}$ , are shown in Fig. 5C. These compare well to experimental radical channel QYs, for energies near to and below the radical channel threshold.

Although the exponential form of  $k_{\text{PPO}}$  fits the CRDS and 1 Bar pressure experimental QY data well, caution should be exercised. Extrapolating to higher energies, the empirical exponential form causes PPO to dominate, exceeding even the unimolecular radical rate, which is unreasonable. Further,  $k_{\text{PPO}}(E)$  must be bounded by the collision encounter rate. At lower energies the empirical form of  $k_{\text{PPO}}$  drops too quickly. The PPO energy threshold is ~13,500 cm<sup>-1</sup> (Fig. 5A), with an entrance channel that is very flat. This suggests, as found in shock tube experiments (39,43), PPO is likely to be efficient, even near threshold. The form of the Maranzana  $k_{\text{PPO}}(E)$  is therefore more reasonable at lower energies. These observations indicate that the energy dependence of  $k_{\text{PPO}}$  is more complex than a single exponential function.

Formaldehyde has two well-known complexities in its dynamics, occurring just below the energy of the radical channel. Firstly, the barrier to isomerisation to hydroxymethylene (CHOH) lies near 30,000 cm<sup>-1</sup> (49,50) with tunnelling reducing the effective barrier. Secondly, the roaming dynamical pathway links the radical and molecular channels, with a threshold about 60 cm<sup>-1</sup> below the radical threshold (51). The roaming mechanism involves a loosely bound H-atom on a flat region of the potential energy surface. Both of these mechanisms provide reasonable



explanations for an increase in  $k_{\text{PPO}}(E)$  over the Maranzana single well calculation, in particular increasing  $k_{\text{PPO}}$  as the radical threshold is approached. A loosely bound H atom can be easily abstracted by  $\text{O}_2$  and  $\text{CHOH}$  can also undergo PPO. Calculation of these additional microcanonical rate coefficients is beyond the scope of the present study.

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Comparison with previous HCHO measurements and atmospheric implications: The previously reported radical quantum yields for excitation of HCHO at  $\lambda > 330$  nm are highly varied and dependent on conditions, as described in SI. Early experiments showed considerable radical yield at long wavelengths, which was then attributed to a lower R1 threshold energy than is now accepted (52-55). In the late 1970s and 80s, when the radical threshold was established close to where it is today (8), the groups of Calvert (18) and Moortgat/Warneck (21, 22) used measurements of CO and  $\text{H}_2$  yields (R2) to infer  $\phi_1$  by difference. Two studies (18, 21) found  $\phi_1 = 0.03$  to 0.05 near 336 nm, reducing to near zero at 340 nm, while the third (22) argued for no radical quantum yield below the R1 threshold. Later, Smith, *et al.* measured the HCO radicals directly, and reported  $\phi_1 = 0.07$  at 336 nm and 0.04 at 339 nm (23). These results are shown in Fig. 5C. In addition, the production of HCOOH following photolysis of HCHO has also been reported previously for  $\lambda > 330$  nm (21,26). No interpretation has been offered for the presence of radicals, nor HCOOH, at photolysis energies below the radical threshold. We propose HCOOH is formed from  $\text{HO}_2$  arising from PPO. Given our observation of the sensitivity of PPO to trace amounts of  $\text{O}_2$  (Fig. 3), the observed quantum yields and observation of HCOOH over many years are broadly consistent with our reported  $\phi_{\text{PPO}}$ .

This work proposes that the radical quantum yields currently used in atmospheric modelling (24) invoke the wrong mechanism for  $\lambda > 330$  nm. However, because the PPO of HCHO produces the same radical species as direct PCO, the implications for tropospheric chemistry will be subtle. The only consequence will be the different pressure dependences of the R1 and R5 pathways; the R1 QY decreases with pressure whereas the R5 QY increases with pressure. For more complex molecules, however, the PCO and PPO mechanisms will produce different radicals, with different consequences.

The photochemical properties of HCHO are not unique nor special other than the simplicity imbued by a small number of atoms. We predict other molecules will have competitive PPO pathways. For example, there is unrecognised evidence of PPO in the photochemistry of acetaldehyde, CH<sub>3</sub>CHO. Morajkar *et al.* used CRDS to investigate HO<sub>2</sub> production following photolysis of CH<sub>3</sub>CHO at 248 nm (56). They identified HO<sub>2</sub> arising via PCO *via* the HCO + CH<sub>3</sub> and CH<sub>3</sub> + CO + H dissociation channels. They also identified a third “rapid HO<sub>2</sub>” pathway with no known mechanism, speculating HO<sub>2</sub> was formed from reaction of O<sub>2</sub> with photo-excited CH<sub>3</sub>CHO. This is a description of the PPO reaction and we propose Morajkar *et al.* measured PPO in CH<sub>3</sub>CHO and that the “energetic CH<sub>3</sub>CHO” speculated in that paper is a highly vibrationally excited S<sub>0</sub> molecule, arising via non-radiative relaxation from the initially excited S<sub>1</sub> CH<sub>3</sub>CHO. Their reported quantum yield of 0.07 is consistent with the  $\phi_{\text{PPO}}$  we have determined for HCHO.

In CH<sub>3</sub>CHO, the dominant PCO pathway is *via* CH<sub>3</sub> + HCO radical channel. PPO would instead lead to CH<sub>3</sub>CO + HO<sub>2</sub> where the acetyl radicals can subsequently form peroxyacetyl nitrate (PAN), especially in urban areas (1,2). As such, the PPO route is more similar to the reaction of CH<sub>3</sub>CHO with OH radicals where the aldehydic H-atom is abstracted to form H<sub>2</sub>O + CH<sub>3</sub>CO. The difference in these mechanisms is that OH reaction results in a net loss of HO<sub>x</sub> radicals (HO<sub>x</sub> = OH + HO<sub>2</sub>) from the atmosphere. Conversely, PPO results in a net gain in HO<sub>x</sub> radicals via direct formation of HO<sub>2</sub>.

We also suggest PPO may be important in carbonyls more generally, and particularly in carbonyls with low photolysis QYs. Such atmospherically important carbonyls include acetone, the highest mostly highly emitted industrial ketone with 44 Tg/yr emitted to the atmosphere (57), and methylvinylketone and methacrolein, which are major oxidation products of isoprene, the largest emitted biogenic compound in the troposphere (58). Many other molecules also satisfy the conditions for PPO, including alkyl- and aryl-nitrates, NO<sub>2</sub> itself, and alkylperoxides. If PPO is occurring in these and other molecules, the implications for tropospheric chemistry include:

- i) Formation of different radicals than previously considered, which may have different subsequent fates and impact. Generally, PPO will produce larger radicals *via* H-abstraction compared to photolysis, which frequently breaks a C-C bond. The larger carbon-centred radicals formed by PPO will react with atmospheric O<sub>2</sub> to form less volatile oxygenated species that are implicated in aerosol formation (*Erreur ! Signet non défini.*).

- ii) Radical formation at lower photon energies, below radical dissociation thresholds. Radicals formed via PPO will affect the modelled mixing ratio of radical chain carriers, for example OH and HO<sub>2</sub>.
- iii) Changes to the vertical profile for radical formation. Photolysis quantum yields quench with increasing pressure, as collisional relaxation competes with unimolecular reaction;  $\phi_{ph}$  are highest at low pressure. However, as a bimolecular reaction, PPO quantum yields will increase with increasing O<sub>2</sub> partial pressure (Fig. 3 and Table S8).

We propose PPO will be a general reaction in atmospheric chemistry. Any molecule that absorbs near-UV light, has small fluorescence and photolysis QYs and has a low energy abstraction pathway for reaction with O<sub>2</sub> is likely to undergo PPO. Many atmospherically prevalent molecules satisfy these criteria including carbonyls, alkyl- and aryl-nitrates, NO<sub>2</sub> itself, and alkylperoxides.

### **Conclusions**

We have identified photophysical oxidation (PPO) in the photochemistry of HCHO in the presence of O<sub>2</sub>. The PPO reaction involves photo-excitation of the parent molecule, its non-radiative transfer to the electronic ground state and subsequent fast reaction with O<sub>2</sub>, before the molecule has a chance to thermalise. PPO is a single elementary reaction and can occur at photon energies below radical dissociation thresholds, whereas conventional photochemical oxidation requires an initial radical photolysis, so can only occur at photon energies above the radical threshold, and refers to multiple elementary reactions. As a bimolecular reaction, the PPO reaction rate increases with O<sub>2</sub> pressure, which is the reverse to normal photolysis, where increased pressure generally quenches the reaction. In the atmosphere, PPO is therefore more important at higher pressures, that is, at lower altitudes, relative to other photochemical processes.

Photophysical oxidation is likely to be a general reaction in tropospheric chemistry and its implications are yet to be explored.

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Writing – review & editing: BW, MC, EA, KN, PS, MJTJ, CF, SHK

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**Data and materials availability:** All data are available in the manuscript or the supplementary materials.

## **Supplementary Materials**

30 Materials and Methods

Supplementary Text

Tables S1 – S8

Figs S1 – S12

Additional References (59-87)

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## References

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1. for example, B. J. Finlayson-Pitts, J. N. Pitts, Jr. *Chemistry of the Upper and Lower Atmosphere – Theory, Experiments, and Applications*, (Academic Press, San Diego, CA, 2000).
2. R. Atkinson, J. Arey, Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* **103**, 4605–4638 (2003). doi.org/10.1021/cr0206420
3. D. R. Glowacki, J. Lockhart, M. A. Blitz, S. J. Klippenstein, M. J. Pilling, S. H. Robertson, P. W. Seakins, Interception of excited vibrational quantum states by O<sub>2</sub> in atmospheric association reactions, *Science*, **337**, 1066 (2012)
4. V. Vaida, D. J. Donaldson, Red-light initiated atmospheric reactions of vibrationally excited molecules, *Phys. Chem. Chem. Phys.* **16**, 827–836 (2014)
5. e.g. J. C. Tully, Reactions of O(<sup>1</sup>D) with atmospheric molecules. *J. Chem. Phys.* **62**, 1893–1898 (1975); doi.org/10.1063/1.430675
6. B. Ruscic and D. H. Bross, Active Thermochemical Tables (ATcT) values based on ver. 1.124 of the Thermochemical Network (2022); available at ATcT.anl.gov; accessed 20 December 2022.
7. P. L. Houston, C. B. Moore, Formaldehyde photochemistry: Appearance rate, vibrational relaxation, and energy distribution of the CO product. *J. Chem. Phys.* **65**, 757–770 (1976). doi.org/10.1063/1.433092
8. M.-C. Chuang, M. F. Foltz, C. B. Moore, *T*<sub>1</sub> barrier height, *S*<sub>1</sub>–*T*<sub>1</sub> intersystem crossing rate, and *S*<sub>0</sub> radical dissociation threshold for HCHO, D<sub>2</sub>CO, and HDCO. *J. Chem. Phys.* **87**, 3855–3864 (1987). doi.org/10.1063/1.452940
9. L. R. Valachovic, M. F. Tuchler, M. Dulligan, Th. Droz-Georget, M. Zyrianov, A. Kolessov, H. Reisler, C. Wittig, Photoinitiated HCHO unimolecular decomposition: Accessing H+HCO products via *S*<sub>0</sub> and *T*<sub>1</sub> pathways. *J. Chem. Phys.* **112**, 2752–2761 (2000). doi.org/10.1063/1.480849
10. D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, J. M. Bowman, The roaming atom: Straying from the reaction path in formaldehyde decomposition. *Science* **306**, 1158–1161 (2004). doi.org/10.1126/science.1104386
11. J. Troe, Analysis of Quantum Yields for the Photolysis of Formaldehyde at  $\lambda > 310$  nm. *J. Phys. Chem. A* **111**, 3868–3874 (2007). doi.org/10.1021/jp066886w
12. M. S. Quinn, K. Nauta, M. J. T. Jordan, J. M. Bowman, P. L. Houston, S. H. Kable, Rotational resonances in the HCHO roaming reaction are revealed by detailed correlations, *Science*, **369**, 1592–1596 (2020). doi.org/10.1126/science.abc4088

- 
13. M. S. Quinn, D. U. Andrews, K. Nauta, M. J. T. Jordan, S. H. Kable, The energy dependence of CO( $v, J$ ) produced from via the transition state, roaming, and triple fragmentation channels. *J. Chem. Phys.* **147**, 013935 (2017). doi.org/10.1063/1.4983138
  14. D. Feller, M. Dupuis, B. C. Garrett, Barrier for the HCHO  $\rightarrow$  H<sub>2</sub> + CO reaction: A discrepancy between high-level electronic structure calculations and experiment. *J. Chem. Phys.* **113**, 218–226, (2000). doi.org/10.1063/1.481788
  15. G. F. Bauerfeldt, L. M.M. de Albuquerque, G. Arbilla, E. C. da Silva, Unimolecular reactions on formaldehyde  $S_0$  PES. *J. Molec. Struct. (Theochem)* **580**, 147–160 (2002). doi.org/10.1016/S0166-1280(01)00609-1
  16. X. Zhang, J. L. Rheinecker, and J. M. Bowman, Quasiclassical trajectory study of formaldehyde unimolecular dissociation: HCHO  $\rightarrow$  H<sub>2</sub> + CO, H + HCO. *J. Chem. Phys.* **122**, 114313 (2005). doi.org/10.1063/1.1872838
  17. L. B. Harding, S. J. Klippenstein, A. W. Jasper, Ab initio methods for reactive potential surfaces. *Phys. Chem. Chem. Phys.* **9**, 4055–4070 (2007). doi.org/10.1039/B705390H
  18. J. H. Clark. C. B. Moore, N. S. Nogar, *J. Chem. Phys.* **68**, 1264–1271 (1978). doi.org/10.1063/1.435848
  19. A. Horowitz, J. G. Calvert, Wavelength dependence of the quantum efficiencies of the primary processes in formaldehyde photolysis at 25°C. *Int. J. Chem. Kin.* **10**, 805–819 (1978). doi.org/10.1002/kin.550100803
  20. G. K. Moortgat, F. Slemr, W. Seiler, P. Warneck, Relative quantum yields of H<sub>2</sub> and CO in the wavelength range 70–360 nm. *Chem. Phys. Lett.* **54**, 444–447 (1978). doi.org/10.1016/0009-2614(78)85257-9
  21. G. K. Moortgat, P. Warneck, CO and H<sub>2</sub> quantum yields in the photodecomposition of formaldehyde in air. *J. Chem. Phys.* **70**, 3639–3651 (1979). doi.org/10.1063/1.437956
  22. G. K. Moortgat, W. Seiler, P. Warneck, Photodissociation of HCHO in air: CO and H<sub>2</sub> quantum yields at 220 and 300 K. *J. Chem. Phys.* **78**, 1185–1190 (1983). doi.org/10.1063/1.444911
  23. G. D. Smith, L. T. Molina, M. J. Molina, Measurement of radical quantum yields from formaldehyde photolysis between 269 and 339 nm. *J. Phys. Chem. A* **106**, 1233–1240 (2002). doi.org/10.1021/jp-13180n
  24. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II gas phase reactions of organic species. *Atmos. Chem. Phys.* **6**, 3625–4055 (2006). doi.org/10.5194/acp-6-3625-2006; IUPAC Subcommittee for Gas Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>). Datasheet updated: 16th April 2013; last change in preferred values: 16th April 2013
  25. J. S. Campbell, K. Nauta, C. S. Hansen, S. H. Kable, POPTARTS: A New Method to Determine Quantum Yields in a Molecular Beam, *J. Phys. Chem. A*, **XX**, XXXX (2022) (published on-line 30-Nov-2022). doi.org/10.1021/acs.jpca.2c06289

- 
26. F. Su, J. G. Calvert, J. H. Shaw, Mechanism of the photooxidation of gaseous formaldehyde. *J. Phys. Chem.* **83**, 3185–3191 (1979). doi.org/10.1021/j100488a001
27. A. C. Terentis, S. E. Waugh, G. F. Metha, S. H. Kable, HCO ( $N$ ,  $K_a$ ,  $K_c$ ,  $J$ ) distributions from near-threshold photolysis of HCHO ( $J$ ,  $K_a$ ,  $K_c$ ). *J. Chem. Phys.* **108**, 3187–3198 (1998). doi.org/10.1063/1.475736
28. E. Assaf, L. Liu, C. Schoemaeker, C. Fittschen, Absorption Spectrum and Absorption Cross Sections of the  $2\nu_1$  band of HO<sub>2</sub> between 20 and 760 Torr Air in the Range 6636 and 6639 cm<sup>-1</sup>. *J. Quant. Spectrosc. & Rad. Transfer* **211**, 107–114 (2018). doi.org/10.1016/j.jqsrt.2018.02.035
29. M. F. Shaw, B. Sztáray, L. K. Whalley, D. E. Heard, D. B. Millet, M. J. T. Jordan, David L. Osborn, S. H. Kable, Photo-tautomerization of acetaldehyde as a photochemical source of formic acid in the troposphere. *Nat. Commun.*, **9**, 2584 (2018). doi.org/10.1038/s41467-018-04824-2
30. D. J. Clouthier, D. A. Ramsay, The spectroscopy of formaldehyde and thioformaldehyde. *Ann. Rev. Phys. Chem.* **34**, 31–58 (1983). doi.org/10.1146/annurev.pc.34.100183.000335
31. M. Motsch, M. Schenk, M. Zeppenfeld, M. Schmitt, W. L. Meerts, P. W. H. Pinkse, G. Rempe, Spectroscopy of the A<sup>1</sup>A<sub>2</sub> - X<sup>1</sup>A<sub>1</sub> transition of formaldehyde in the 30140 – 30790 cm<sup>-1</sup> range: The 2<sup>1</sup><sub>0</sub>4<sup>3</sup><sub>0</sub> and 2<sup>2</sup><sub>0</sub>4<sup>1</sup><sub>0</sub> rovibrational bands. *J. Molec. Spectrosc.* **252**, 25–30 (2008). doi.org/10.1016/j.jms.2008.06.002
32. M. E. Jenkin, M. D. Hurley, T. J. Wallington, Investigation of the radical product channel of the CH<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub> reaction in the gas phase. *Phys. Chem. Chem. Phys.* **9**, 3149–3162 (2007). doi.org/10.1039/B702757E
33. P. Morajkar, C. Schoemaeker, M. Okumura, C. Fittschen, Direct measurement of the equilibrium constants of the reaction of formaldehyde and acetaldehyde with HO<sub>2</sub> radicals. *Int. J. Chem. Kin.* **46**, 245–259 (2014). doi.org/10.1002/kin.20817
34. M. Bixon, J. Jortner, Intramolecular radiationless transitions. *J. Chem. Phys.* **48**, 715–726 (1968). doi.org/10.1063/1.1668703
35. J. C. Weisshaar, C. B. Moore, Isotope, electric field, and vibrational state dependence of single rotational level lifetimes of S<sub>1</sub> formaldehyde. *J. Chem. Phys.* **72**, 5415–5425 (1980). doi.org/10.1063/1.439036
36. H. M. Yin, S. H. Kable, X. Zhang, J. M. Bowman, Signatures of HCHO photodissociation from two electronic states. *Science* **311**, 1443–1446 (2006). doi.org/10.1126/science.1123397
37. R. G. Miller, E. K. C. Lee, Single vibronic level photochemistry of formaldehydes in the  $\tilde{A}^1A_2$  state: Radiative and nonradiative processes in HCHO, HDCO, and D<sub>2</sub>CO. *J. Chem. Phys.* **68**, 4448–4464 (1978). doi.org/10.1063/1.435527
38. L. K. Huynh, M. Tirtowidjojo, T. N. Truong, Theoretical study on kinetics of the HCHO + O<sub>2</sub> → HCO + HO<sub>2</sub> reaction. *Chem. Phys. Lett.* **469**, 81–84 (2009). doi.org/10.1016/j.cplett.2008.12.050

- 
39. J. V. Michael, S. S. Kumaran, M.-C. Su, Rate constants for  $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$  at high temperature and evidence for  $\text{HCHO} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2$ . *J. Phys. Chem. A* **103**, 5942–5948 (1999). doi.org/10.1021/jp9909457
40. V. Vasudevan, D. F. Davidson, R. K. Hanson, C. T. Bowman, D. M. Golden, High-temperature measurements of the rates of the reactions  $\text{CH}_2\text{O} + \text{Ar} \rightarrow \text{products}$  and  $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{products}$ . *Proc. Comb. Inst.* **31**, 175–183 (2007). doi.org/10.1016/j.proci.2006.07.017
41. Y. Hidaka, T. Taniguchi, H. Tanaka, T. Kamesawa, K. Inami, H. Kawano, Shock-tube study of  $\text{CH}_2\text{O}$  pyrolysis and oxidation. *Combust. Flame* **92**, 365–376 (1993). doi.org/10.1016/0010-2180(93)90149-W
42. B. Eiteneer, C.-L. Yu, M. Goldenberg, M. Frenklach, Determination of rate coefficients for reactions of formaldehyde pyrolysis and oxidation in the gas phase. *J. Phys. Chem. A* **102**, 5196–5205 (1998). doi.org/10.1021/jp981184v
43. N. K. Srinivasan, M.-C. Su, J. W. Sutherland, J. V. Michael, Reflected shock tube studies of high-temperature rate constants for  $\text{CH}_3 + \text{O}_2$ ,  $\text{HCHO} + \text{O}_2$ , and  $\text{OH} + \text{O}_2$ . *J. Phys. Chem. A*, **109**, 7902–7914 (2005). doi.org/10.1021/jp0581330
44. D. Feller, M. Dupuis B. C. Garrett, Barrier for the reaction: A discrepancy between high-level electronic structure calculations and experiment *J. Chem. Phys.* **113**, 218–226 (2000); doi.org/10.1063/1.481788
45. A. Maranzana, J. R. Barker, G. Tonachini, Master equation simulations of competing unimolecular and bimolecular reactions: application to OH production in the reaction of acetyl radical with  $\text{O}_2$ . *Phys. Chem. Chem. Phys.* **9**, 4129–4141 (2007). doi.org/10.1039/b705116f
46. J. R. Barker, T. L. Nguyen, J. F. Stanton, C. Aieta, M. Ceotto, F. Gabas, T. J. D. Kumar, C. G. L. Li, L. L. Lohr, A. Maranzana, N. F. Ortiz, J. M. Preses, J. M. Simmie, J. A. Sonk, and P. J. Stimac; MultiWell-2022 Software Suite; J. R. Barker, University of Michigan, Ann Arbor, Michigan, USA, 2022; <http://clasp-research.engin.umich.edu/multiwell/>.
47. J. R. Barker, Multiple-Well, multiple-path unimolecular reaction systems. I. MultiWell computer program suite. *Int. J. Chem. Kinetics*, **33**, 232–245 (2001). doi.org/10.1002/kin.1017
48. J. R. Barker, Energy transfer in master equation simulations: A new approach. *Int. J. Chem. Kinetics*, **41**, 748–763 (2009). doi.org/10.1002/kin.20447
49. X. Zhang, S. Zou, L. B. Harding, J. M. Bowman, A Global *ab Initio* Potential Energy Surface for Formaldehyde, *J. Phys. Chem. A* **108**, 8980–8986 (2004).
50. S. Maeda, K. Ohno, K. Morokuma, Automated global mapping of minimal energy points on seams of crossing by the anharmonic downward distortion following method: A case study of  $\text{H}_2\text{CO}$ , *J. Phys. Chem. A*, **113**, 1704–1710 (2009). doi.org/10.1021/jp810898u
51. S. A. Lahankar, S. D. Chambreau, X. Zhang, J. M. Bowman, A. G. Suits, Energy dependence of the roaming atom pathway in formaldehyde decomposition, *J. Chem. Phys.* **126**, 044314 (2007). doi.org/10.1063/1.2429660



- 
52. R. Klein, L. J. Schoen, Photodecomposition of formaldehyde; stability of the HCO radical. *J. Chem. Phys.* **24**, 1094-1096 (1956). doi.org/10.1063/1.1742685
53. M. Venugopalan, K. O. Kutschke, The photolysis of formaldehyde-d<sub>2</sub>, formaldehyde and their mixtures. *Can. J. Chem.* **42**, 2451-2455 (1964). doi.org/10.1139/v64-360
54. R. D. McQuigg, J. G. Calvert, Photodecomposition of CH<sub>2</sub>O, CD<sub>2</sub>O, CHDO, and CH<sub>2</sub>O-CD<sub>2</sub>O mixtures at xenon flash lamp intensities. *J. Am. Chem. Soc.* **91**, 1590-1599 (1969). doi.org/10.1021/ja01035a002
55. H. P. Sperlberg, S. Toby, The photochemical decomposition of gaseous formaldehyde. *Can. J. Chem.* **51**, 471-475 (1973). doi.org/10.1139/v73-072
56. P. Morajkar, A. Bossolasco, C. Schoemaeker, C. Fittschen, Photolysis of CH<sub>3</sub>CHO at 248 nm: Evidence of triple fragmentation from primary quantum yield of CH<sub>3</sub> and HCO radicals and H atoms. *J. Chem. Phys.* **140**, 214308 (2014). doi.org/10.1063/1.4878668
57. A. B. Guenther, X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, X. Wang, The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev.* **5**, 1471-1492 (2012). doi.org/10.5194/gmd-5-1471-2012
58. P. O. Wennberg, K. H. Bates, J. D. Crouse, L. G. Dodson, R. C. McVay, L. A. Mertens, T. B. Nguyen, E. Praske, R. H. Schwantes, M. D. Smarte, J. M. St Clair, A. P. Teng, X. Zhang, J. H. Seinfeld, Gas-phase reactions of isoprene and its major oxidation products. *Chem Rev.* **118**, 3337-3390 (2018). doi.org/10.1021/acs.chemrev.7b00439
59. M. Staak, E. W. Gash, D. S. Venables, A. A. Ruth, The rotationally-resolved absorption spectrum of formaldehyde from 6547 to 6804 cm<sup>-1</sup>, *J. Mol. Spectrosc.* **229**, 115-121 (2005). doi.org/10.1016/j.jms.2004.08.019
60. A. A. Ruth, U. Heitmann, E. Heinecke, C. Fittschen, C., The rotationally resolved absorption spectrum of formaldehyde from 6547 to 7051 cm<sup>-1</sup>, *Z. Phys. Chem.* **229**, 1609-1624 (2015). doi.org/10.1515/zpch-2015-0623
61. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
62. D. G. Truhlar, R. Steckler, and M. S. Gordon, Potential energy surfaces for polyatomic reaction dynamics, *Chem. Rev.* **87**, 217-236 (1987). doi.org/10.1021/cr00077a011
63. J. L. Durant, Evaluation of transition state properties by density functional theory, *Chem. Phys. Lett.* **256**, 595-602 (1996). doi.org/10.1016/0009-2614(96)00478-2

- 
64. M. F. Shaw, Photochemical Formation of Enols from Carbonyls. (Ph.D. Thesis, The University of Sydney, 2017).
65. K. N. H. Rowell, S. H. Kable, M. J. T. Jordan, An assessment of the tropospherically accessible photo-initiated ground state chemistry of organic carbonyls *Atmos. Chem. Phys.* **2022**, 929–949 (2022). doi.org/10.5194/acp-22-929-2022
66. M. L. Laury, S. E Boesch, I. Haken, P. Sinha, M. J. Carlson, A. K. Wilson, Harmonic vibrational frequencies: scale factors for pure, hybrid, hybrid meta, and double-hybrid functionals in conjunction with correlation consistent basis sets. *J. Comp. Chem.* **32**, 2339–2347 (2011). doi.org/10.1002/jcc.21811
67. M. K. Kesharwani, B. Brauer, J. M. L. Martin, Frequency and zero-point vibrational energy scale factors for double-hybrid density functionals (and other selected methods): Can anharmonic force fields be avoided? *J. Phys. Chem. A* **119**, 1701–1714 (2015). doi.org/10.1021/jp508422u
68. NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 21, August 2020, Editor: R. D. Johnson III <http://cccbdb.nist.gov/> accessed 1 March 2021.
69. K. G. Lubic, T. Amano, H. Uehara, K. Kawaguchi, E. Hirota, The  $\nu_1$  band of the DO<sub>2</sub> radical by difference frequency laser and diode laser spectroscopy: The equilibrium structure of the hydroperoxyl radical, *J. Chem. Phys.* **81**, 4826–4831 (1984). doi.org/10.1063/1.447508
70. G. Herzberg, Electronic spectra and electronic structure of polyatomic molecules (Van Nostrand Reinhold, New York, 1966).
71. K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
72. J. L. Duncan, The ground-state average and equilibrium structures of formaldehyde and ethylene, *Mol. Phys.* **28**, 1177–1191 (1974). doi.org/10.1080/00268977400102501
73. K. N. Rowell, S. H. Kable, M. J. T. Jordan, Structural effects on the Norrish Type I  $\alpha$ -bond cleavage of tropospherically important carbonyls. *J. Phys. Chem. A*, **123**, 10381–10396 (2019). doi.org/10.1021/acs.jpca.9b05534
74. C. M. Western, PGOPHER, A Program for Simulating Rotational, Vibrational and Electronic Spectra. *J Quant. Spectrosc Rad. Transfer*, **186** 221–242 (2017). doi.org/10.1016/j.jqsrt.2016.04.010
75. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species. *Atmos. Chem. Phys.*, **4**, 1461–1738 (2004). doi.org/10.5194/acp-4-1461-2004
76. C. A. Smith, F. D. Pope, B. Cronin, C. B. Parkes, and A. J. Orr-Ewing, Absorption cross sections of formaldehyde at wavelengths from 300 to 340 nm and at 294 and 245 K, *J. Phys. Chem. A* **110**, 11645–11653 (2006). doi.org/10.1021/jp063713y
77. K. Chance and J. Orphal, Revised ultraviolet absorption cross sections of HCHO for the HITRAN database, *J. Quant. Spectrosc. Radiat. Transfer* **112**, 1509–1510 (2011). doi.org/10.1016/j.jqsrt.2011.02.

- 
78. S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, G. K. Moortgat, H. Keller-Rudek, P. H. Wine, A. R. Ravishankara, C. E. Kolb, M. J. Molina, B. J. Finlayson-Pitts, V. L. Orking Orking, Chemical kinetics and photochemical data for use in atmospheric studies NASA JPL Evaluation No. 15JPL Publication 06-2 (2006).
79. D. C. Tardy, B. S. Rabinovitch, Intermolecular vibrational energy transfer in thermal unimolecular systems. *Chem. Rev.* **77**, 369-408 (1977). doi.org/10.1021/cr60307a004
80. A. B. Weaver, A. A. Alexeenko, Revised Variable Soft Sphere and Lennard-Jones Model Parameters for Eight Common Gases up to 2200 K. *J. Phys. Chem. Ref. Data* **44**, 023103 (2015). doi.org/10.1063/1.4921245.
81. J. Troe, Mixture Rules in Thermal Unimolecular Reactions. *Ber. Bunsenges. Phys. Chem.* **84**, 829-834, (1980). doi.org/10.1002/bbpc.19800840902
82. J. R. Barker, L. M. Yoder, K. D. King, Vibrational energy transfer modeling of non-equilibrium polyatomic reaction systems. *J. Phys. Chem. A* **105**, 796-809 (2001). doi.org/10.1021/jp002077f
83. A. W. Jasper, "Third-body" collision parameters for hydrocarbons, alcohols, and hydroperoxides and an effective internal rotor approach for estimating them. *Int J Chem Kinet.* **52**, 387-402 (2020). doi.org/10.1002/kin.21358
84. S. J. Klippenstein, An efficient procedure for evaluating the number of available states within a variably defined reaction coordinate framework. *J. Phys. Chem.* **98**, 11459-11464 (1994). doi.org/10.1021/j100095a032
85. K. L. K. Lee, M. S. Quinn, S. J. Kolmann, S. H. Kable, M. J. T. Jordan, Zero-point energy conservation in classical trajectory simulations: Application to H<sub>2</sub>CO, *J. Chem. Phys.* **148**, 194113 (2018). doi.org/10.1063/1.5023508
86. A. W. Jasper, C. M. Oana, J. A. Miller, "Third-Body" collision efficiencies for combustion modeling: Hydrocarbons in atomic and diatomic baths *Proc. Combust. Inst.* **35**, 197-2040 (2015). doi.org/10.1016/j.proci.2014.05.105
87. A. W. Jasper, J. A. Miller, Theoretical Unimolecular Kinetics for CH<sub>4</sub> + M ⇌ CH<sub>3</sub> + H + M in Eight Baths, M = He, Ne, Ar, Kr, H<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub>. *J. Phys. Chem. A* **115**, 6438-6455 (2011). doi.org/10.1021/jp200048n