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Sunlight-driven combustion of HCHO in the troposphere: Photophysical Oxidation of HCHO produces HO₂ 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 O₂ to form HO₂. In this paper, we report direct experimental detection of HO₂ 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 HO₂ at 1 Bar pressure through the detection of formic acid, a product from secondary HO₂ 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 O₂. 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 O₂. 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 HO₂ and OH radicals then initiate further radical chain reactions that cleanse the atmosphere of most pollutants and oxidise atmospheric carbon to CO₂ (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, NO₃ or O₃, 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 O₂ 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 H₂SO₄ can explain the SO₂ 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 ¹D electronic state react facily with important atmospheric molecules, such as H₂O and N₂O, whereas ground state O(³P) 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, S₁. Internal conversion (IC) transfers the energy to the ground electronic state, S₀. 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_2 to initiate photophysical oxidation (PPO), forming HCO and HO_2 radicals. In the case of HCHO, the critical threshold energy for PPO (161 kJ mol^{-1} , (6)) is less than half of that required for PCO via radical formation from direct photolysis of the C-H bond ($362.8 \text{ kJ mol}^{-1}$).

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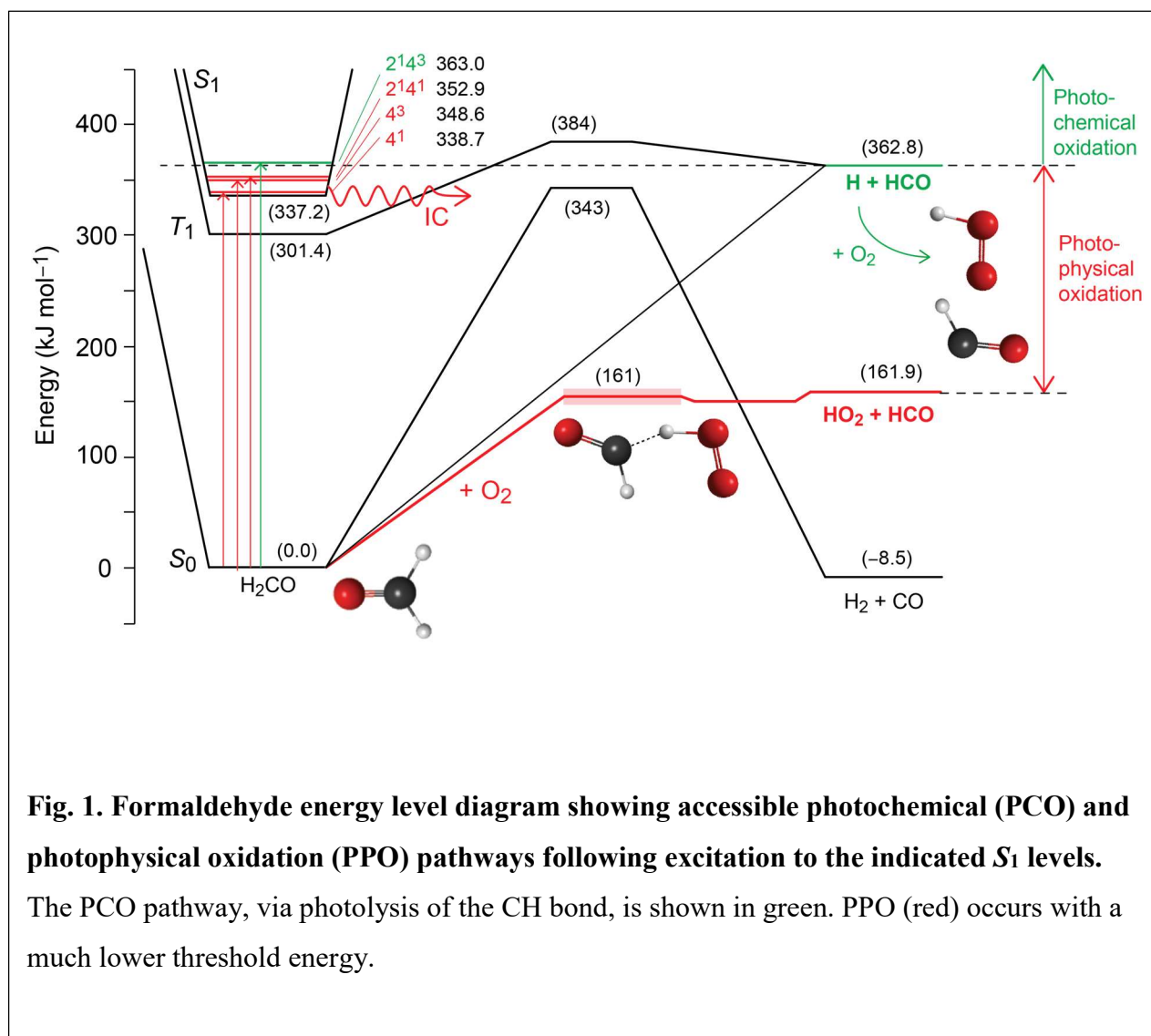


Fig. 1. Formaldehyde energy level diagram showing accessible photochemical (PCO) and photophysical oxidation (PPO) pathways following excitation to the indicated S_1 levels. The PCO pathway, via photolysis of the CH bond, is shown in green. PPO (red) occurs with a much lower threshold energy.

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), ϕ_{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_2 to produce $\text{HO}_2\bullet$:



where M is a collision partner needed to stabilise $\text{HO}_2\bullet$. 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⁻¹ (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, ϕ_{ph} is less than unity and pressure dependent (18-22); there is competition between R2 and collisions with (mainly) N₂ and O₂, which remove excess vibrational energy and return HCHO to thermal equilibrium. Here,
10 we demonstrate that these collisions with O₂ can also lead to PPO of HCHO:



15 where the double dagger represents vibrationally-activated HCHO.

Results

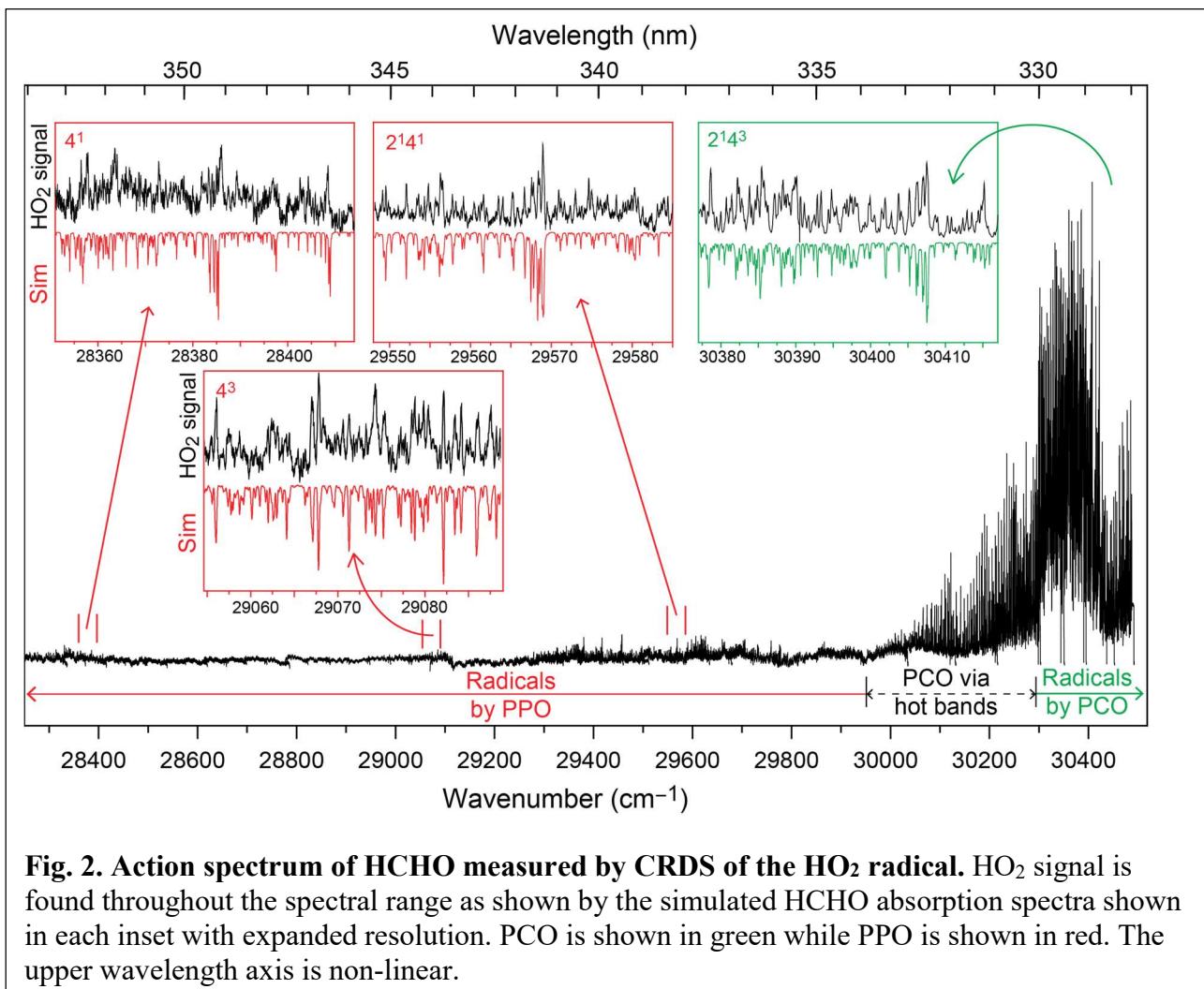
We employed two experimental techniques, with interpretation supported by *ab initio* electronic structure theory calculations of the critical energies of R5 and Master Equation kinetic modelling
20 of PPO under experimental conditions. In both experiments, a laser was used to excite specific vibrational levels of the *S*₁ 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, 4¹, 4³ and 2¹4¹ lie 24, 14 and 10 kJ/mol below the radical threshold, respectively, while the higher
25 lying level, 2¹4³, is 0.2 kJ mol⁻¹ above the radical threshold. The 4¹ 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 HO₂, following HCHO irradiation in the presence of O₂. 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 HO₂ 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 HO₂: Figure 2 shows a CRDS action spectrum, where HO₂ 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 HO₂ via R3 and R4. The inset panels also have clearly assigned HCHO structure, shown in red, where

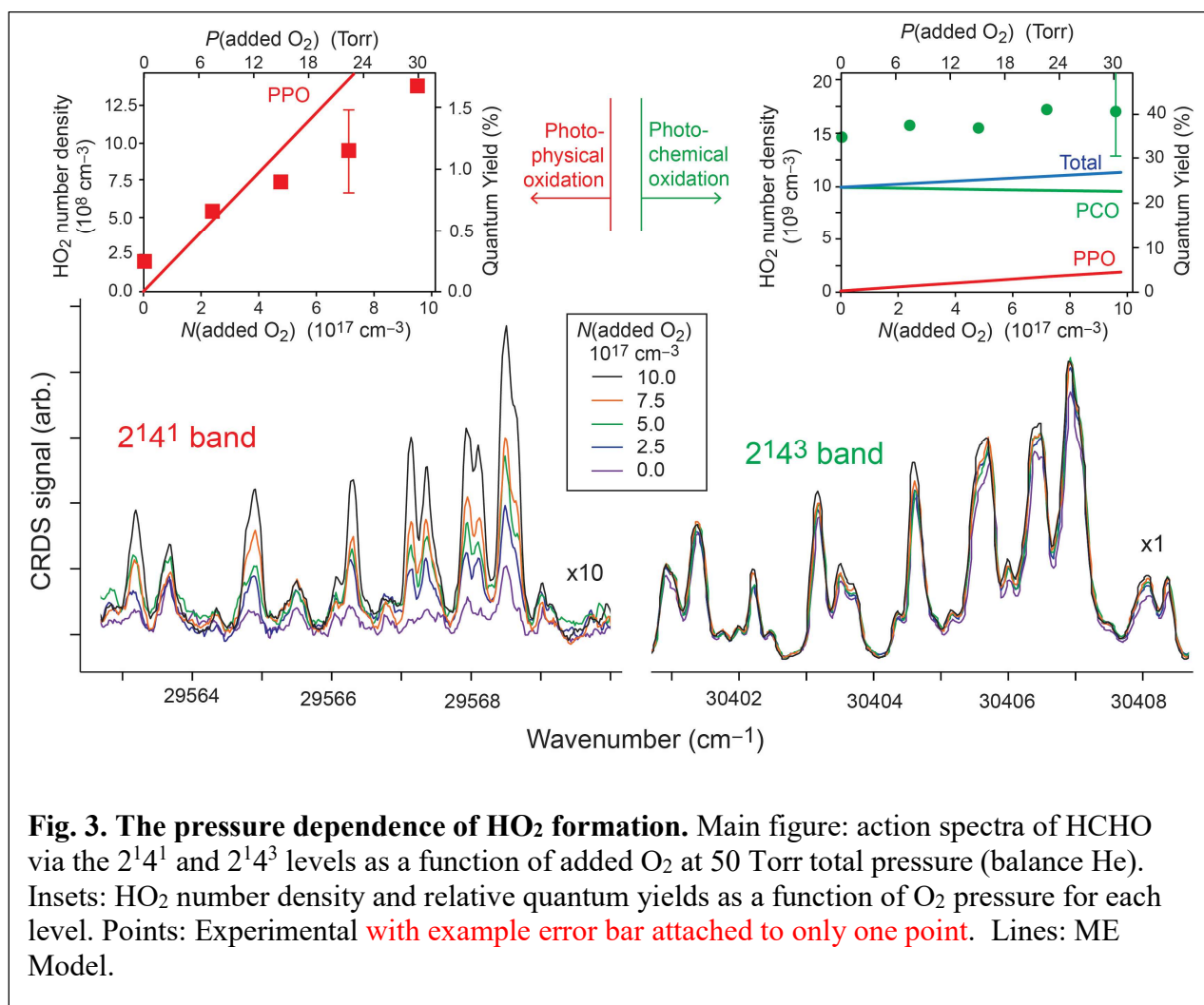


PCO production of HO₂ is not energetically possible. This is the region of photophysical production of HO₂. The signal-to-noise ratio for excitation to the 4³ and, especially, 4¹ levels is

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 HO₂ signal on O₂ pressure at a total pressure of 50 Torr (balance helium) is shown in Fig. 3. The HO₂ 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 O₂ pressure are key observations of this work and indicate a new bimolecular chemical mechanism for radical formation.

The HO₂ signal above the radical threshold ($2^1_4^3$) shows a small increase with increasing O₂ pressure. The observed HO₂ at $P(\text{added O}_2) = 0$ is due to background O₂, which we estimate from the measured leak rate as $\sim 10^{14} \text{ cm}^{-3}$ (3 mTorr). Because the background O₂ 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 HO₂ via R3 and R4, that is, via

the conventional PCO mechanism. The slight increase in HO₂ as *P*(added O₂) is increased may be due to the presence of the PPO channel (R5) and/or reduced diffusion of H-atoms and HO₂ 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 (2¹4¹, below the photochemical threshold for radical formation), as well as diluted in 160 Torr N₂, 160 Torr O₂ and 760 Torr synthetic air (79% N₂, 21% O₂). 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 4¹ (352.48 nm) and 2¹4³ (329.06 nm) levels in synthetic air are shown in Fig. S1. The FTIR spectra for neat HCHO photolysis, and in the presence of N₂, show only CO, which is formed via R2 (the H₂ co-product does not absorb IR light). The FTIR product spectra taken in the
15 presence of O₂ 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 HO₂ 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 2¹4¹ and 4¹ levels in 760 Torr synthetic air (Figs 4 and S1, respectively), confirms production of HO₂, 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 O₂. The CRDS experiments demonstrate HO₂ is formed at energies up to 24 kJ mol⁻¹ 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 HO₂ and the

parent HCHO. The linear dependence of HO₂ with O₂ concentration seen in the CRDS experiments implies a bimolecular reaction between photo-excited HCHO and O₂.

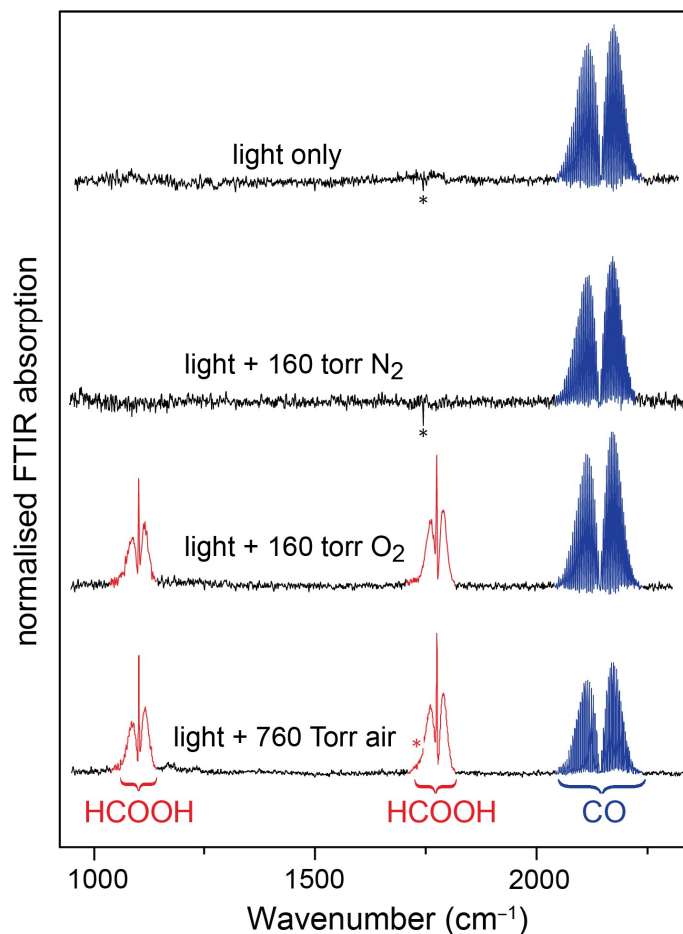


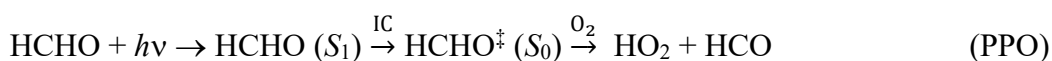
Fig. 4: FTIR spectra of reaction end products following excitation of 1 Torr HCHO to the $2^1_4^1$ level in different buffer gases as indicated. Spectra are on the same scale but displaced vertically for presentation. HCOOH is only formed in the presence of O₂. **The asterisks show where a sharp residual 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 O₂: *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 HO₂ 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 HO₂, 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 O₂ with HCHO (S_1) correlates with HCO in the electronically excited $\tilde{A}(^2A')$ state. Although the HCO(\tilde{A}) + HO₂ 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 HO₂ 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 ‡) and O₂:



HCHO ‡ has extremely high, non-thermal, vibrational energy arising from absorption of a photon but all other degrees of freedom, including the HCHO and O₂ 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 O₂ 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⁻¹, with a recommended zero-point corrected value of 161.4 kJ mol⁻¹, 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 O₂ in- and out-of-plane rotation, that is, O₂ 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 ϕ_{PPO} in CRDS experiments by internal calibration. Above the R1 threshold, photo-excitation results in two HO₂ 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 HO₂ radicals, via R5 and R4. We calculate ϕ_{PPO} from the ratio of the observed HO₂ number density following excitation of the lower energy levels, compared to the 2¹4³ level. The HCHO absorption cross-section for each transition is known and corrected for, which then yields the wavelength-dependent QY, ϕ_{PPO} . At 30 Torr added O₂, we determine $\phi_{\text{PPO}} = 0.017 \pm 0.005$ at 338 nm (2¹4¹), 0.025 ± 0.010 at 343 nm (4³) and 0.014 ± 0.007 at 352 nm (4¹), where the uncertainty arises from the combined uncertainty of the fit to literature absorption spectra and the uncertainty in the literature QY of the 2¹4³ 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, HO₂ 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 HO₂ 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, H₂ + CO and HCO + HO₂.

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⁻¹ (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_{PPO} from first principles, and a top-down empirical approach fitting k_{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_{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 N₂ and O₂ 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 N₂ and O₂ and $\langle \Delta E_{\text{down}} \rangle = 25 \text{ cm}^{-1}$ for collisions of S_1 HCHO with N₂ and O₂, reflecting the sparse density of states in S_1 . The ME
30 simulations were run with 150,000 stochastic trials for 1.0 μs , 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.

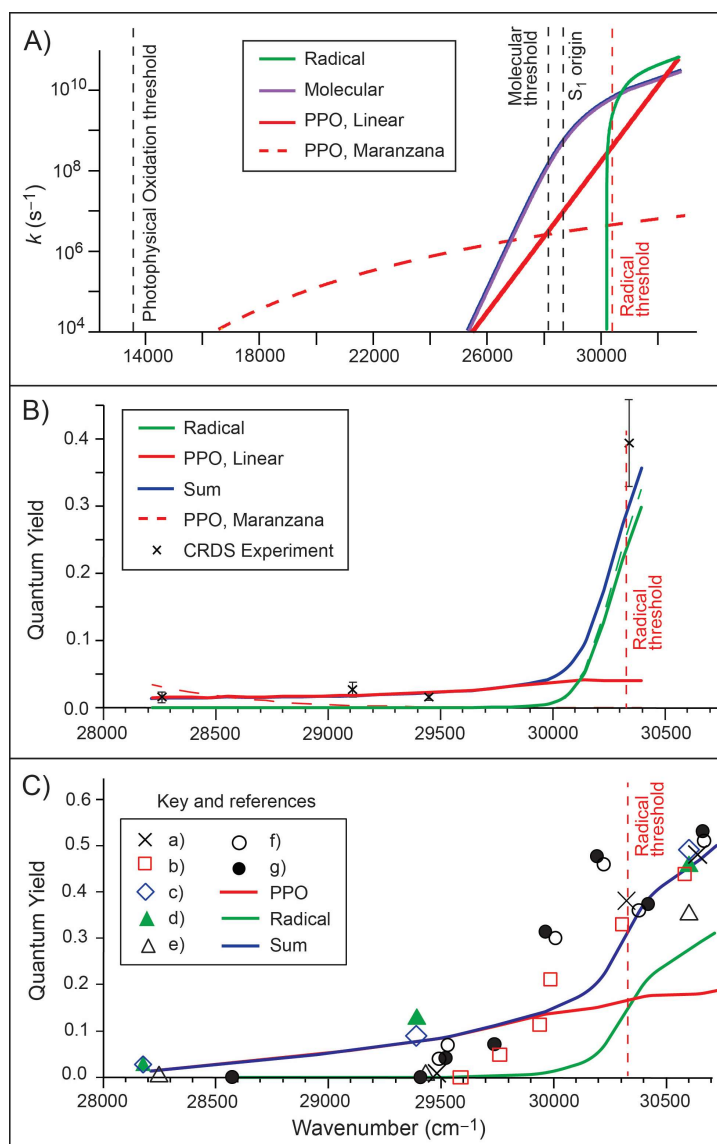


Fig. 5: Energy dependence of rate coefficients and quantum yields. A) First order, microscopic rate coefficients used in Master Equation calculations. The PPO rate coefficient is pseudo first order for 30 Torr O₂. B) Quantum yields for various processes in CRDS experiments at 30 Torr added O₂. C) Quantum 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 O₂, 20 Torr He. The Maranzana form (45) of the PPO rate coefficient yields ϕ_{PPO} that is close to experiment at the lowest 4¹ level.

5 However ϕ_{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_{PPO} . This is not in accord with the experimental findings.

The energy-dependent HO₂ QYs obtained with k_{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 2¹4³ energy.

The ME simulations have also been used to predict the O₂ pressure dependence of the HO₂ QY (Fig. 3 and Table S8). The observed CRDS pressure dependence is modelled well, using the fitted k_{PPO} , with the strong linear increase in HO₂ QY with pressure reproduced for states below the radical threshold. The ME simulations also predict a much weaker linear increase in HO₂ QY with pressure for the 2¹4³ state, where PCO via the radical channel products dominates HO₂ 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_{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_{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_{PPO} drops too quickly. The PPO energy threshold is ~13,500 cm⁻¹ (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_{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⁻¹ (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⁻¹ 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_{PPO} as the radical threshold is approached. A loosely bound H atom can be easily abstracted by O_2 and CHOH can also undergo PPO. Calculation of these additional microcanonical rate coefficients is beyond the scope of the present study.

5 .

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/Warnecke (21, 22) used measurements of CO and H_2 yields (R2) to infer ϕ_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 HO_2 arising from PPO. Given our observation of the sensitivity of PPO to trace amounts of O_2 (Fig. 3), the observed quantum yields and observation of HCOOH over many years are broadly consistent with our reported ϕ_{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, CH₃CHO. Morajkar *et al.* used CRDS to investigate HO₂ production following photolysis of CH₃CHO at 248 nm (56). They identified HO₂ arising via PCO *via* the HCO + CH₃ and CH₃ + CO + H dissociation channels. They also identified a third “rapid HO₂” pathway with no known mechanism, speculating HO₂ was formed from reaction of O₂ with photo-excited CH₃CHO. This is a description of the PPO reaction and we propose Morajkar *et al.* measured PPO in CH₃CHO and that the “energetic CH₃CHO” speculated in that paper is a highly vibrationally excited S₀ molecule, arising via non-radiative relaxation from the initially excited S₁ CH₃CHO. Their reported quantum yield of 0.07 is consistent with the ϕ_{PPO} we have determined for HCHO.

In CH₃CHO, the dominant PCO pathway is *via* CH₃ + HCO radical channel. PPO would instead lead to CH₃CO + HO₂ 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 CH₃CHO with OH radicals where the aldehydic H-atom is abstracted to form H₂O + CH₃CO. The difference in these mechanisms is that OH reaction results in a net loss of HO_x radicals (HO_x = OH + HO₂) from the atmosphere. Conversely, PPO results in a net gain in HO_x radicals via direct formation of HO₂.

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, NO₂ 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 O₂ 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 HO₂.
- iii) Changes to the vertical profile for radical formation. Photolysis quantum yields quench with increasing pressure, as collisional relaxation competes with unimolecular reaction; ϕ_{ph} are highest at low pressure. However, as a bimolecular reaction, PPO quantum yields will increase with increasing O₂ 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 O₂ is likely to undergo PPO. Many atmospherically prevalent molecules satisfy these criteria including carbonyls, alkyl- and aryl-nitrates, NO₂ itself, and alkylperoxides.

Conclusions

We have identified photophysical oxidation (PPO) in the photochemistry of HCHO in the presence of O₂. The PPO reaction involves photo-excitation of the parent molecule, its non-radiative transfer to the electronic ground state and subsequent fast reaction with O₂, 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 O₂ 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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15

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Supplementary Materials

30 Materials and Methods

Supplementary Text

Tables S1 – S8

Figs S1 – S12

Additional References (59-87)

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