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PHOTOCHEMISTRY

Photophysical oxidation of atmospheric carbonyls

Light is a major driver of the chemistry of the atmosphere and usually involves the photolytic fragmentation of molecules into radicals prior to their reaction. Now, Jordan, Kable and colleagues have shown that formaldehyde, excited by low-energy light, can react with oxygen opening up alternative atmospheric oxidation pathways.

Paul W. Seakins

Carbonyl species are important intermediates in atmospheric chemistry. Their absorption of solar radiation, at photon energies above the threshold for bond dissociation, can lead to the formation of radical species. For a generic aldehyde, RCHO, this can be represented as:

$$\mathrm{RCHO} + h\nu \rightarrow \mathrm{R} + \mathrm{HCO} \qquad \text{(P1)}$$

P1 is usually in competition with carbonyl removal by reaction by OH radicals:

$$\mathrm{RCHO} + \mathrm{OH} \rightarrow \mathrm{RCO} + \mathrm{H_2O} \qquad \text{(R1)}$$

Now Jordan, Kable and colleagues[1] have observed an additional process, that they call photophysical oxidation (PPO), in which the carbonyl absorbs lower energy light (not enough to make it fragment) producing an excited molecule, $\mathrm{RCHO}^{\ddagger}$. In the atmosphere, this excited species can then react with oxygen – a process that is in competition with relaxation back to the ground state.

$$\mathrm{RCHO} + h\nu \rightarrow \mathrm{RHCO}^{\ddagger} \qquad \text{(P2)}$$

$$\mathrm{RHCO}^{\ddagger} + \mathrm{O_2} \rightarrow \mathrm{RCO} + \mathrm{HO_2} \qquad \text{(R2)}$$

When modelling most systems, we assume that the products of one reaction or photolysis process have regained their thermal equilibrium before they become the reagents of a subsequent reaction. Jordan, Kable and colleagues have observed a system in which that is not the case. They show that, in the presence of oxygen, absorption of a photon by formaldehyde, the simplest carbonyl species, with energy less than that of the threshold to radical dissociation (P3), still leads to the production of radical species. They suggest that following absorption of a photon to the excited S_1 state (Fig 1), there is a fast internal conversion to the S_0 ground state; then reaction of the vibrationally excited HCHO molecule ($\mathrm{HCHO(S_0)}^{\ddagger}$) with O_2 (R3) to radical products occurs on a second potential energy surface (PES). This reaction is in competition with vibrational relaxation to the equilibrium distribution (R4). For formaldehyde, the first-generation products for both direct photolysis above the radical threshold (P3) and PPO (P3,R4) are CO and HO_2 due to the fast reactions R5 and R6.

The research by Jordan, Kable and colleagues highlights the best of current, sophisticated experimental techniques, but also the importance of tried and tested instrumentation, supporting experimental work with calculations and, additionally, the information that can be extracted from older literature.

Clear evidence for PPO comes from experiments where the energetics are defined and precise excitation from a high-resolution dye laser determines the energy level of HCHO accessed in the S_1 state. The HO_2 product from reaction R1 is detected by direct, sensitive, *in situ* cavity ring down spectroscopy measurements, so that there is no ambiguity from either sampling or specificity issues. Jordan, Kable and colleagues measure an action spectrum for HO_2 production, which is monitored as the laser exciting the formaldehyde is slowly scanned. HO_2 is only observed when the excitation laser exactly matches a transition to a specific vibration/rotation state in the S_1 state of HCHO. Following the peaks in HO_2 production maps out a spectrum that corresponds well to simulations of HCHO excitation confirming that HO_2 is being produced from HCHO and not any impurities, and that HO_2 is being produced at excitation wavelengths at which direct photolysis cannot occur. As mentioned above, there is competition between R3 and vibrational relaxation to the equilibrium distribution (R4) and Jordan, Kable and colleagues showed that, as would be expected, increasing the amount of O_2, increases the fraction of $HCHO^{\ddagger}$ that is converted to HO_2.

Complementary to these relatively sophisticated experiments is the use of FTIR detection of formic acid, HC(O)OH, via (R7) to confirm the presence of HO_2 radical products following low-energy excitation of HCHO (P1).

$$HO_2 + HCHO \rightarrow\rightarrow HCOOH \qquad \text{(R7)}$$

While the FTIR methods cannot provide quantitative quantum yields for PPO, they do confirm that PPO occurs at 1 atmosphere of air, demonstrating that there is potential for atmospheric impact.

Jordan, Kable and colleagues support their experimental observations with a range of theoretical approaches, firstly, looking at the PES for the reaction of $HCHO^{\ddagger}$ with O_2 using *ab initio* methods. Whilst the calculated barrier height does depend on the method used, all values (151 – 175 kJ mol^{-1}) are well below the excitation energy, therefore even after several non-reactive collisions with the bath gas, there will still be sufficient energy in the $HCHO^{\ddagger}$ to allow for the PPO reaction to occur efficiently. Secondly, they use master equation methods to model this competition between the PPO reaction on the HCHO + O_2 PES and relaxation on the HCHO PES, as a function of total pressure and the partial pressure of oxygen. Their master equation calculations are in good agreement with experiment.

Finally, the results of Jordan, Kable and colleagues agree with earlier studies, which, while they may have lacked the ability to detect HO_2, their indirect, end-product analysis provides support for the current measurements. These earlier results are examples of the wealth of observational data present in the literature. Turanyi and co-workers[2], working in the combustion field, are currently trying to bring together, within the framework of a chemical model, disparate data recorded using different conditions, equipment and focused on different goals (e.g. elementary reactions in a chemical process or the overall process). There is scope for this approach to be used more widely, particularly as data mining techniques improve.

Chemical reactions can also be the source of non-equilibrium reactants. Addition or recombination reactions, as exemplified by the work of Glowacki et al.[3], are clear candidates for non-equilibrium effects as all the reaction exothermicity is channelled into a single product. Abstraction reactions, producing two products are more common processes. However, despite the reaction exothermicity being split between products, chemically activated processes have been observed[4,5,6].

Whether the activated species is produced by photolysis or chemical reaction, vibrational relaxation to thermalized species will be rapid so that, in general, unimolecular reactions on a second potential energy surface are most likely to compete with relaxation. However, bimolecular reactions with O_2 can compete in regimes with high concentrations of O_2 for example in the atmosphere and during combustion.

A key question is whether PPO has a significant impact on atmospheric chemistry. Jordan, Kable and colleagues note that the products of PPO and photolysis (P1) are the same for formaldehyde, but this will not be the case for most carbonyls. PPO promotes the formation of radicals analogous to those produced from OH abstraction, whereas conventional photolysis results in C-C fragmentation. They also found that the quantum yields for PPO were significantly lower than those for conventional photolysis, however, two factors can still promote the importance of PPO. Firstly, there are many examples of non-linearity in atmospheric chemistry, such that, relatively small changes in one process, can result in substantial overall changes. Secondly, as shown schematically in Figure 2a, thresholds for radical formation from direct solar photolysis are close to the highest energy photos that reach the, troposphere, the lower portion of the atmosphere, whereas PPO will occur at longer wavelengths, where the solar flux into the troposphere is increasing rapidly, off-setting the less efficient quantum yields for PPO.

The wider impact of PPO will need to be considered by in-depth modelling and experimental studies that are beyond the scope of this initial study. The barrier for abstraction of an H by O_2 from a ketone species is likely to be greater than for an aldehyde, so how will PPO be affected? How does PPO scale with increasing size and complexity of the carbonyl species? The energy of the system and the barrier to overcome in reaction R2 will remain similar as the size of the molecule increases, however this energy is distributed over a larger number of vibrations, which means that stabilization is more likely to win out. Methacrolein, a key intermediate in the oxidation of isoprene (the most abundant hydocarbon emission into the atmosphere), is suggested as a good candidate for PPO. Gierczak et al.[7] studied the fate of methacrolein under atmospheric conditions. Methacrolein was photolysed at 351 nm (a photon energy well below dissociation threshold) in the presence of oxygen and a small photolysis quantum yield of 0.005 was observed, supporting PPO, but at levels smaller than that observed for HCHO – possibly indicative that PPO decreases with size. Figure 2B explores the potential atmospheric impact of PPO in slightly more detail for aldehydes.

Experimental evidence for non-equilibrium chemistry on multiple potential energy surfaces initiated by a variety of processes is coming into the literature. The chemistry itself is interesting and provides important insights into mechanisms of reaction. Currently the jury is out as to whether there is widespread impact in key systems such as combustion and atmospheric chemistry, but many aspects of combustion and atmospheric chemistry, such as chain branching and nucleation have non-linear components, so that small changes, induced for example by PPO, can have significant effects. It will be interesting to see over the next few years how the status of non-equilibrium chemistry evolves.

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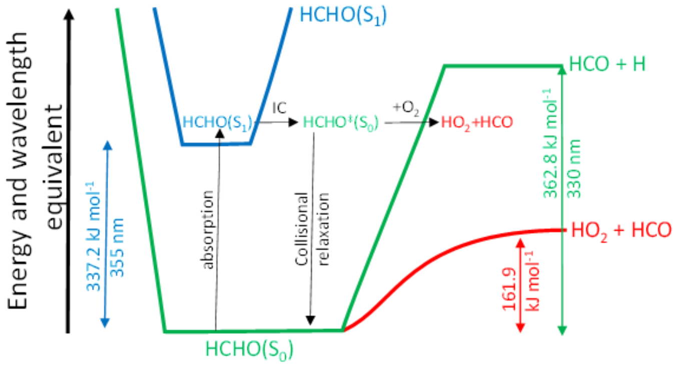

$HCHO + h\nu \rightarrow H + HCO$ (P3)

$HCHO + h\nu \rightarrow HCHO(S_1) \rightarrow HCHO(S_0)^{\ddagger}$ (P4)

$HCHO(S_0)^{\ddagger} + O_2 \rightarrow HO_2 + HCO$ (R3)

$HCHO(S_0)^{\ddagger} + M \rightarrow HCHO + M$ (R4)

$HCO + O_2 \rightarrow HO_2 + CO$ (R5)

$H + O_2 \rightarrow HO_2$ (R6)

Figure 1. Pathways for photochemical oxidation of formaldehyde. a) Simplified potential energy surface for photolysis (green) and PPO (red) of HCHO highlighting the threshold wavelengths for photolysis and PPO b) Reactions involved in the photochemical oxidation of formaldehyde

$HCHO + h\nu \rightarrow H + HCO$ (P3)

$HCHO + h\nu \rightarrow HCHO(S_1) \rightarrow HCHO(S_0)^{\ddagger}$ (P4)

$HCHO(S_0)^{\ddagger} + O_2 \rightarrow HO_2 + HCO$ (R3)

$HCHO(S_0)^{\ddagger} + M \rightarrow HCHO + M$ (R4)

$HCO + O_2 \rightarrow HO_2 + CO$ (R5)

$H + O_2 \rightarrow HO_2$ (R6)

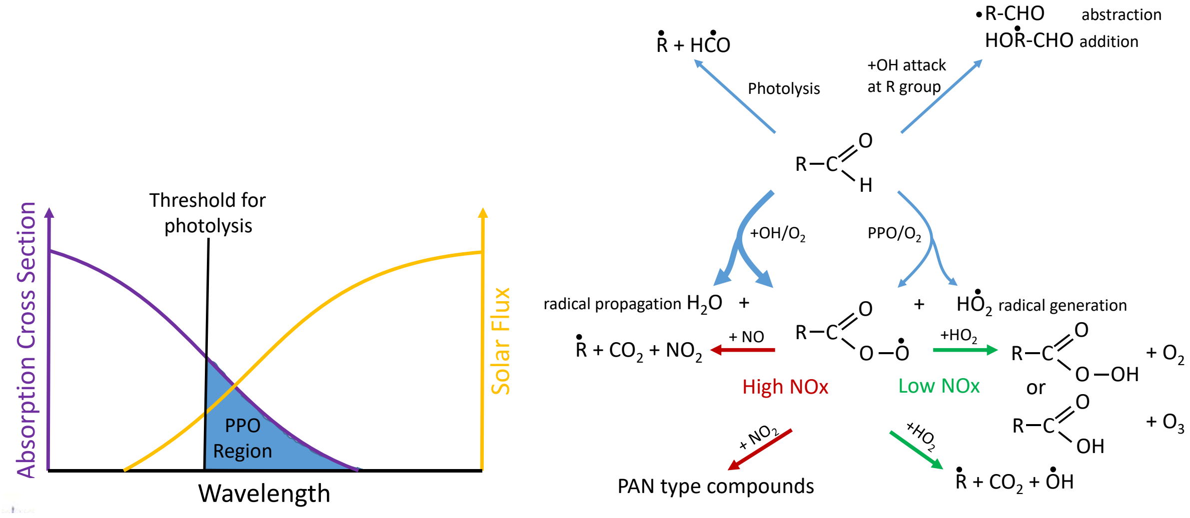

Figure 2 . **a.** Schematic showing the variation in absorption cross section and solar flux with wavelength for a generic aldehyde. The absorption cross section for a generic ketone is blue shifted enhancing the potential for PPO. **b.** Atmospheric fates of a generic aldehyde R-CHO. Direct photolysis results in a loss of functionality as the carbonyl moiety is separated from any functionality in the R group (e.g. a C=C bond in methacrolein). Impact then depends on the relative rate of formation of $RC(O)O_2$ from PPO vs OH, and on the abstraction environment. In urban environments with high concentration of NO, $RC(O)O_2$ is mainly converted to R + CO_2 (typically >95%) but a small fraction of $RC(O)O_2$ reacts with NO forming toxic peroxyacyl-nitrate-type compounds. The fate of $RC(O)O_2$ is far more interesting in environments with low concentration of NO, where reaction with HO_2 radicals is a key loss process, and low volatility acids and peracids can be formed. Such species are of importance in nucleation and the formation of aerosols.[8]

Competing interests The author declares no competing interests.