A new source of $HO_2^\bullet$?

Photophysical Oxidation (PPO) in the Atmosphere

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I. Motivation: a missing source of $HO_2^\bullet$?

- Welsh et al.[1] reported experimental evidence for ***photophysical oxidation*** (PPO) of CH_2O, where vibrationally-activated CH_2O* reacts with O_2 to form radicals after excitation at energies less than the threshold for photochemical oxidation (PCO) (Fig. 1).
- Formaldehyde (CH_2O) can degrade via PPO forming HO_2 (Table 1)
- **Theoretical calculations[2] show other carbonyls**, including acetaldehyde (CH_3CHO), **can also degrade via PPO**, with different products than from PCO (Table 2).
- Acetaldehyde PPO produces peroxy acetyl radical ($CH_3CO_3^\bullet$), with potential implications for peroxy acetyl nitrate (PAN) production.

Table 1. *Net reaction from formaldehyde PCO vs PPO[3].*

Photochemical oxidation	(PCO)	Photophysical oxidation	(PPO)
$HCHO + h\nu \rightarrow HCO^\bullet + H$	(6.1)	$HCHO + h\nu \rightarrow HCHO^*$	(6.2)
$H^\bullet + O_2 \rightarrow HO_2^\bullet$	(6.3)	$HCHO^* + O_2 \rightarrow HCO^\bullet + HO_2^\bullet$	(6.4)
$HCO^\bullet + O_2 \rightarrow HO_2^\bullet + CO$	(6.5)	$HCO^\bullet + O_2 \rightarrow HO_2^\bullet + CO$	(6.6)
Net PCO reaction		Net PPO reaction	
$HCHO + h\nu + 2O_2 \rightarrow 2HO_2^\bullet + CO$	(6.7)	$HCHO + h\nu + 2O_2 \rightarrow 2HO_2^\bullet + CO$	(6.8)

Table 2. *Net reaction from acetaldehyde PCO vs PPO[3].*

Photochemical oxidation	(PCO)	Photophysical oxidation	(PPO)
$CH_3CHO + h\nu \rightarrow CH_3^\bullet + HCO^\bullet$	(6.9)	$CH_3CHO + h\nu \rightarrow CH_3CHO^*$	(6.10)
$HCO^\bullet + O_2 \rightarrow HO_2^\bullet + CO$	(6.11)	$CH_3CHO^* + O_2 \rightarrow CH_3CO^\bullet + HO_2^\bullet$	(6.12)
$CH_3^\bullet + O_2 \rightarrow CH_3O_2^\bullet$	(6.13)	$CH_3CO^\bullet + O_2 \rightarrow CH_3CO_3^\bullet + HO_2^\bullet$	(6.14)
Net PCO reaction		Net PPO reaction	
$CH_3CHO + h\nu + 2O_2 \rightarrow CH_3O_2^\bullet + HO_2^\bullet + CO$	(6.15)	$CH_3CHO + h\nu + 2O_2 \rightarrow CH_3CO_3^\bullet + HO_2^\bullet$	(6.16)

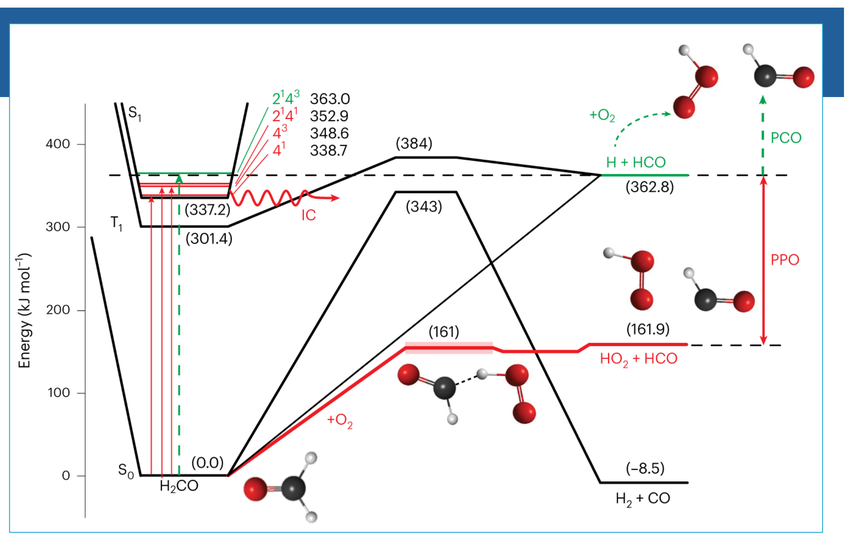

Figure 1. *Energy level diagram for CH_2O PPO (red) and PCO (green) pathways.[1]*

Key Question: Is the atmospheric PPO an important source of $HO_2^\bullet$?

II. Methodology: Global model simulation of formaldehyde and acetaldehyde

- GEOS-Chem v14.3.0. 3-D formaldehyde (CH_2O) and acetaldehyde (CH_3CHO) 1-month simulations.
- Assessing formaldehyde photolysis in GEOS-Chem for wavelengths between 338 and 356 nm. (Fig.2)
- Three potential acetaldehyde PCO channels (Fig. 3), but 6.9b is not energetically accessible.
- GEOS-Chem currently includes 12% molar yield of $CH_3CO_3^\bullet$ inferred from observation of CO_2 formation[5] and erroneously attributed to channel 6.9c – we now understand this to be PPO (with molar yield = 12% consistent with observed quantum yield = 0.07[6]).
- We evaluate the difference between model simulations:
  - including formaldehyde QY_{PPO} = 0.05 for 338 < λ < 356 nm (Fig.2)
  - removing acetaldehyde PPO photolytic contribution for 340 < λ < 363 nm (Fig.5).

CH_2O

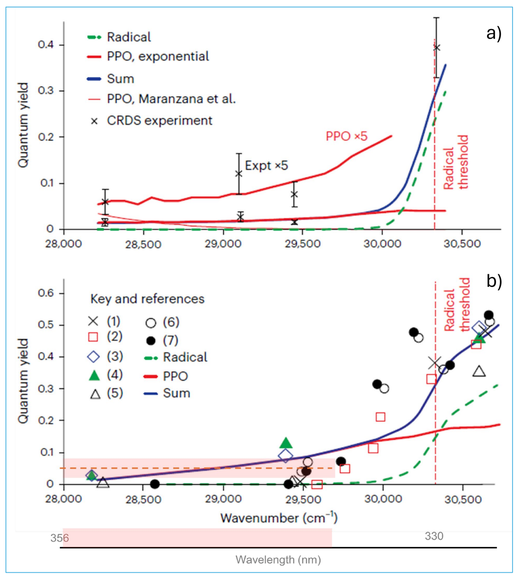

Figure 2. *a) Experimental evidence (CRDS)[1] of HO_2 signal under radical threshold energy. b) Calculated formaldehyde PPO contribution below 30,300 cm^{-1}.*

CH_3CHO

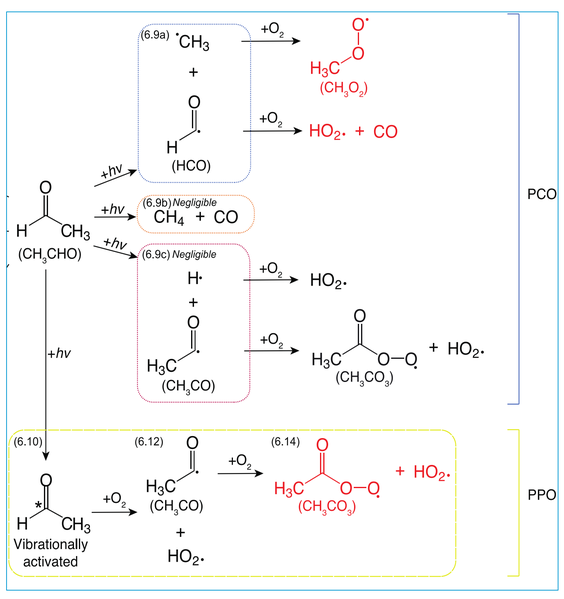

Figure 3. *CH_3CHO photolysis[3]*

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$CH_2O + h\nu$	$\rightarrow H^\bullet + H^\bullet + CO$	423 kJ mol^{-1}	
	$\rightarrow H^\bullet + HCO^\bullet$	363 kJ mol^{-1}	
	$\rightarrow H_2 + CO$	331 kJ mol^{-1}	
Corrigan[2] $CH_2O + h\nu + 2O_2 \rightarrow 2HO_2^\bullet + CO$		163 kJ mol^{-1}	(PPO)

IUPAC[4]

$CH_3CHO + h\nu$	$\rightarrow CH_3CO^\bullet + H^\bullet$	373 kJ mol^{-1}	
	$\rightarrow {}^\bullet CH_3 + HCO^\bullet$	355 kJ mol^{-1}	
Corrigan[2] $CH_3CHO + h\nu + 2O_2 \rightarrow HO_2^\bullet + CH_3CO_3^\bullet$		168 kJ mol^{-1}	(PPO)

Figure 4. *Threshold energies*

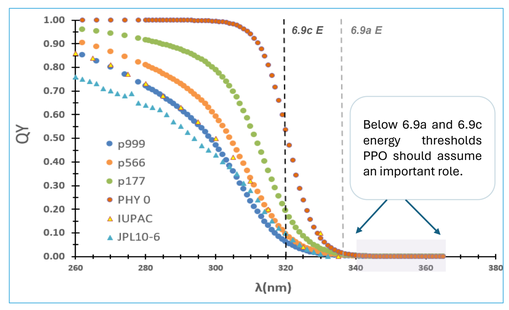

Figure 5. *CH_3CHO QY Pressure dependence*

III. Results

CH_2O

- Adding QY_{PPO} = 0.05, for 338 < λ < 356 nm, in CH_2O radical dissociation path produced a +0.163 % increase in [$HO_2^\bullet$] and -1.148 % decrease for [CH_2O] (1-month simulations (lev=0) are shown in Fig.6 and 7).
- Switching off CH_2O photolysis radical path between 331 and 338 nm (PPO domain) produced a -0.047 % decrease in [$HO_2^\bullet$] and +0.234 % increase in [CH_2O] (not shown).

CH_3CHO

- Change in [$HO_2^\bullet$] attributable to the acetaldehyde PPO in the range 340 < λ < 363 nm is small: -6.22×10^{-6} of % change. (1-month simulations (lev=0) are shown in Fig.8).
- Similar behavior can be observed for [CH_3CHO]: + 0.002 % change (1-month simulations (lev=0) are shown in Fig.9).
- Using a different approach, Perez Pena[3] showed that acetaldehyde PPO contributes on average only 0.6% of total global tropospheric $CH_3CO_3^\bullet$ production, compared to ~38% from CH_3CHO + OH and that change in PAN production attributable to PPO is <2% everywhere (not shown).

CH_2O

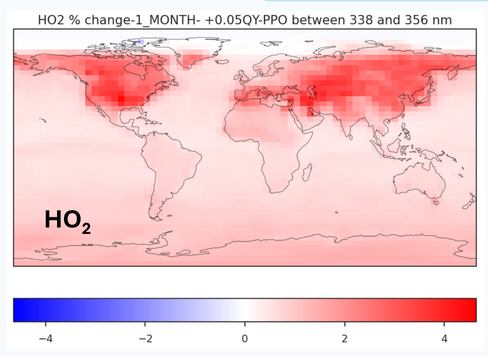

Figure 6. [$HO_2^\bullet$] % change adding 5% PPO. 1-month sim, lev = 0

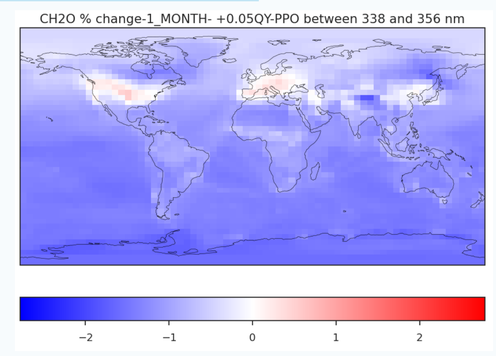

Figure 7. [CH_2O] % change adding 5% PPO 1-month sim, lev = 0

CH_3CHO

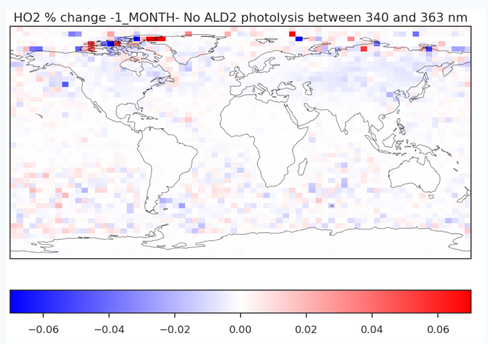

Figure 8. [$HO_2^\bullet$] % change removing acetaldehyde photolysis between 340 and 363 nm. 1-month sim, lev = 0

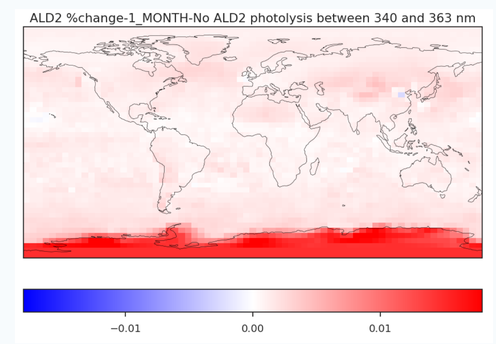

Figure 9. [CH_3CHO] % change removing acetaldehyde photolysis between 340 and 363 nm. 1-month, lev = 0

IV. Take-home messages and future work

- **PPO is a missing source of [$HO_2^\bullet$], but 1-month GEOS-Chem simulations show the impacts from individual species are small.**
- **Theoretical calculations[2] show other carbonyls and several other molecular species con go through PPO, making the sum of contributions to [$HO_2^\bullet$] changes potentially atmospherically relevant.**
- **Future model experiments will target combined effects of PPO from multiple species, impacts of wavelength dependency, and implications of reverse pressure dependence of PPO relative to PCO.**

References: *[1]Welsh et al. (2023), doi: 10.1038/s41557-023-01272-4; [2]Corrigan (2021), PhD Thesis; [3]Perez Pena, (2023), PhD Thesis; [4]Atkinson et al. (2004), IUPAC Data Sheet P2; [5]Moortgat et al. (2010), doi: 10.1002/cphc.201000757; [6] Morajkar et al. (2014), doi: 10.1063/1.4878668*

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Flame tree
Artwork by Samantha Hill
Dharawal/ Wandandian woman

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