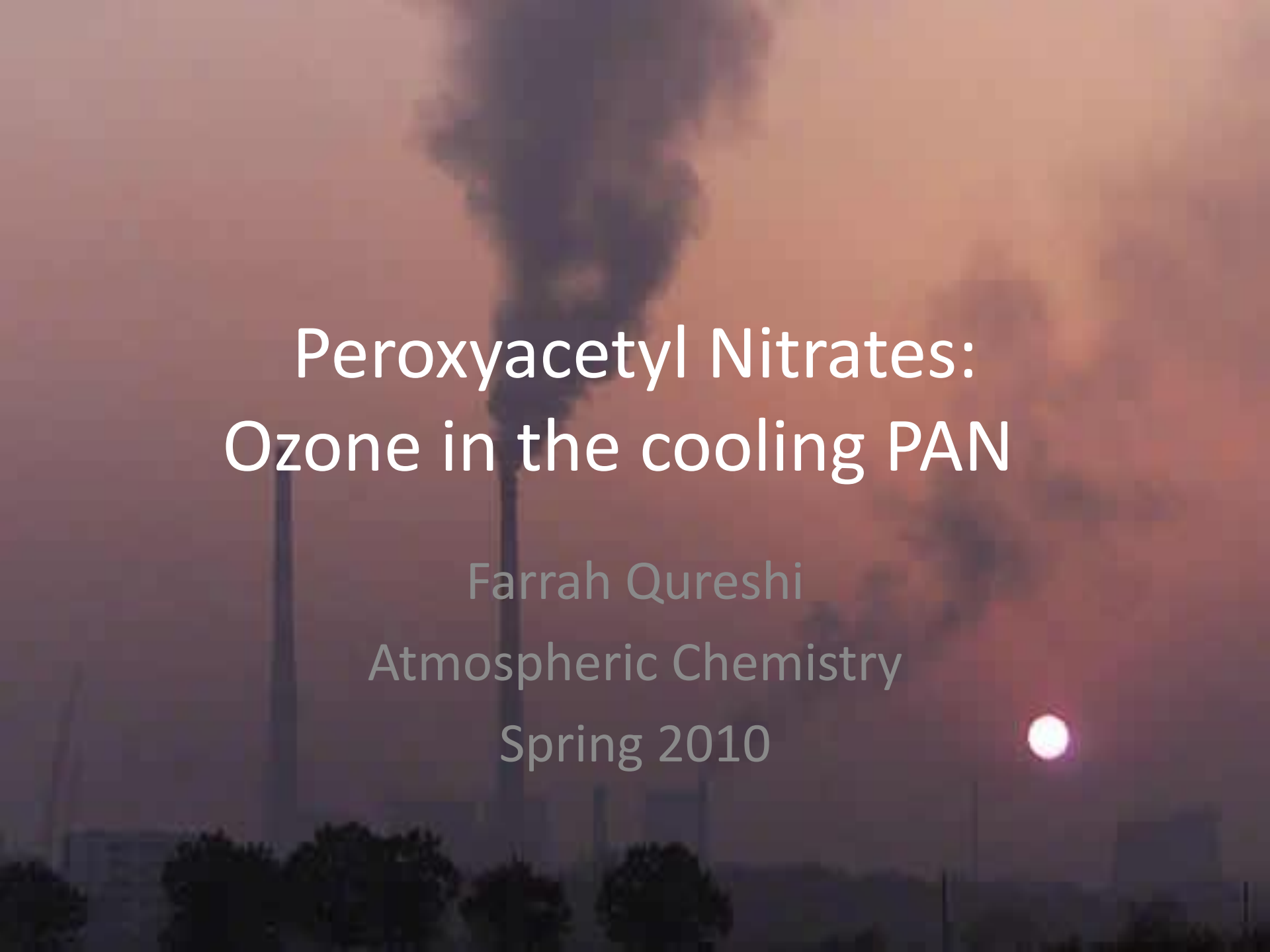

Peroxyacetyl Nitrates: Ozone in the cooling PAN

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Atmospheric Chemistry

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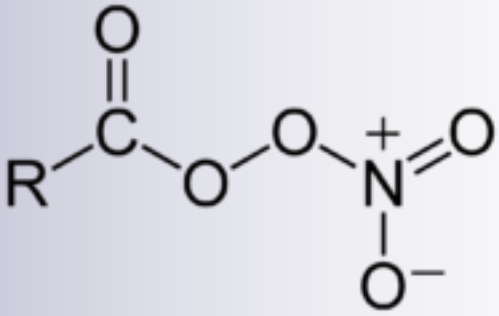
History

- In southern California, farmers noticed that crops and rubber products were deteriorating. Some oxidants were suspected.
- John Middleton first recorded that SO2 and HF (which were postulated to cause this) did not cause the damage; instead of reduction, it was oxidation that caused this damage.
- This area was notorious for its air pollution
- A Perfumery chemist, Arie Haagen-Smit, at Caltech noticed that the smog smelled like the terpenes (a type of hydrocarbon usually produced by plants) in his lab.
- Ellis Darley from UCE exposed various plants to a wide range of chemicals to determine what caused the bronzing with no success.
- Haagen-Smit also fumigated some plants, but did so when he performed an ozonolysis reaction on gasoline. He theorized that the bronzing of foliage was caused by partially ozonized hydrocarbons!
  - Suggested that olefins/alkenes (a molecule with at least one double bond) were responsible for this
  - Suspected causes:
    - Automobiles and oil refineries

The discovery

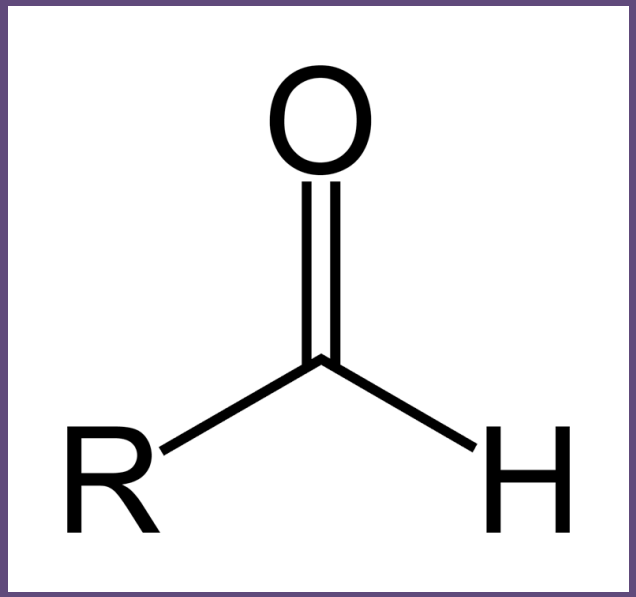
- Researchers from the Franklin Institute Laboratories (Stephens, Hanst, Doerr, and Scott) used long path infrared gas cell to identify products
  - It allowed probing of the IR spectrum of the alkene-NOx mixture
    - 1954
- Found a “compound X”
  - IR spectrum indicated that there were strong bands at 1740 cm^-1 and 1841 cm^-1
  - Found when 3-methylpentane reacted with biacetyl
  - Could not isolate; caused violent reaction
  - Shuck and Doyle synthesized acyl nitrate which had similarities to the nitrate, but was not identical to compound X IR

- Edgar stephens finally produced the correct structure for compound X: peroxyacyl nitrate

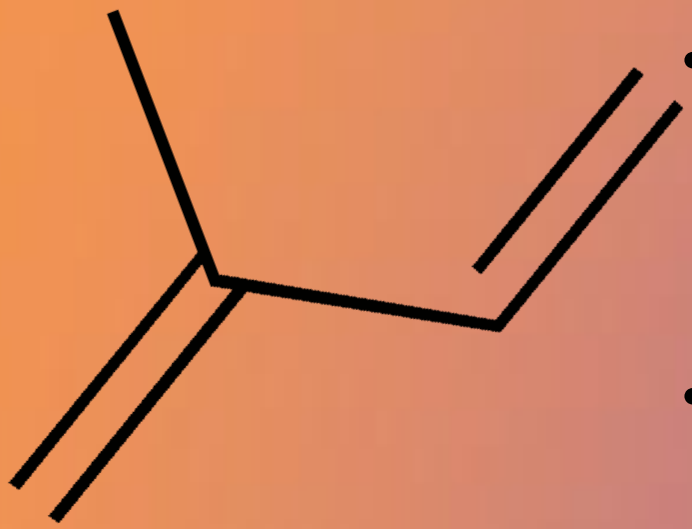


Peroxyacetyl Nitrate formation

- Hydrocarbon chains form aldehydes as an intermediate; hydroxyl attacks and forms acyl; other reaction with hydroxyl forms peroxyacyl radical.
- Reacts with NOx
  - More energetically favorable to react with NO than NO2
- Mechanism with acetaldehyde:
  - CH3CHO + OH → CH3CO +H2O
  - CH3CO +O2 → CH3CO-O-O
  - CH2CO-O-O +NO2 ,←→ CH3CO-O-O-NO2 (PAN!)



Where does this come from?



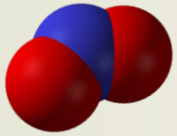
- Naturally, it comes from the degradation of isoprene
  - Isoprene the building blocks of terpenes
- From anthropogenic sources it comes from the degradation of hydrocarbons, acylation, reactions with OH*, and NOx from automobile exhaust and refineries
- Studies suggest that using blended gasoline with ethanol increases PAN; NOx increases with 10% ethanol

Reaction Mechanisms

- $CH_3CO\text{-}O\text{-}O + NO \rightarrow CH_3CO\text{-}O + NO_2$
- $CH_3CO\text{-}O \rightarrow CH_3 + CO_2$
- $CH_3 + O_2 \rightarrow CH_3O_2$
- $CH_3O_2 + NO \rightarrow CH_3O + NO_2$
- $CH_3O + O_2 \rightarrow CH_2O + HO_2$
- $CH_2O + h\nu \rightarrow CO + H_2$
- $\rightarrow HCO + H \rightarrow (O_2) \rightarrow 2\ HO_2 + CO$
- $HO_2 + NO \rightarrow OH + NO_2$

How NOx usually reacts

- $NO_2 + h\nu \rightarrow O(^3P)$ [ground state] + NO
- $O(^3P) + O_2 \rightarrow O_3$



- How does the presence of hydrocarbons affect this?
  - $NO + RO_2^* \rightarrow NO_2 + RO^*$
- What does this imply?
  - PANs, through the formation of NO_2, are responsible for tropospheric ozone creation!

What does PAN do for me?

- Damages plants, art, people, and anything affected by free radicals
  - Causes decay of foliage and skin because of high oxidant power
- Very powerful lachrymator
- PAN and its analogs are 10-50x more toxic than ozone.
- Can react explosively
- Plays a very large role in photochemical smog
- Very stable in colder temperatures
  - Life of PAN 1.7 hrs at 20 C
  - 50 hrs at O C
  - 105 days at -20 C
    - Implications?
      - Can move to the layers of the upper atmosphere and last a very long time
      - Can transport NO2 very long distances; globally important

More PAN impact

- PAN leads to a slight mutagenic effect based on an Ames test conducted on *Salmonella typhimurium* when exposed to low concentrations of PAN
- Trajectories of “Asian air” indicate that PAN, as well as other atmospheric chemicals were transported from Asia to the United States based on chromatographic data

PAN and policy

- Originally mentioned in the Clean Air Act of 1970 along with hydrogen peroxide and NO_2 because there were difficulties measuring and synthesizing standards

Ways to analyze PAN

- Electron Capture Detector (ECD)
  - Use a nonpolar column to separate PANS fro other gases present (such as organo-nitrates, Freon, oxygen, etc.)
  - Had difficulties with said process
- Luminol chemiluminescence
    - Fast capillary chromatography
- Mass spectroscopy
- NMR
- IR
- But NOT UV-Vis spectroscopy

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