

The Influence of Nitrogen Oxides on the Atmospheric Ozone Content

P. J. Crutzen 1970

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Outline

- 1 Prof. Paul Jozef Crutzen
 - Personal, Academic Studies
 - Noble Prize
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 - Change of Odd Oxygen
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Paul Jozef Crutzen



<http://nobelprize.org...>

Personal

- Born December, 3, 1933 in Amsterdam Holland
- Married, two children

Academic Studies

- Civil Engineering, 1951–1954, Amsterdam, Holland.
- Academic Studies and Research Activities 1959–1973 at the University of Stockholm, Sweden.

The Nobel Prize in Chemistry 1995

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"



Paul Jozef Crutzen
*1933
the Netherlands



Mario José Molina
*1943 (Mexico City)
USA



F. S. Rowland
*1927
USA

Balance of O_3

Odd Oxygen

- balance between atomic oxygen and ozone
- reaction is too slow to balance the O_3
- Equation: (5), (7), (8)

OH and HO_2

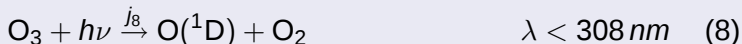
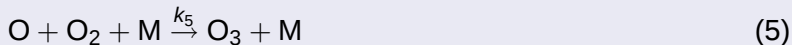
- destruction of ozone by OH or HO_2
- this hypothesis does not explain the ozone observation
- Equation: (14), $HO_2 + O_3$ not used (very speculative)

Odd Nitrogen (NO and NO_2)

- direct controlling effect on the ozone $\Rightarrow$ controlling the ozone production rates
- Equation: (1), (2), (3)

Odd Oxygen

Reactions



Rate Constants

$$k_5 = 8 \cdot 10^{-35} e^{(445/T)} \frac{\text{cm}^3}{\text{s}}$$

$$j_7 = ?$$

$$j_8 = ?$$

$$k_5 : k_0^{300} = 6.0 \cdot 10^{-34}, n = 2.4$$

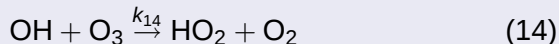
$$j_7 = ?$$

$$j_{8\infty} = 7.8 \cdot 10^{-3} \frac{1}{\text{s}}$$

left: [Crutzen, 1970], right: [Sander, 2006] & [Brasseur & Solomon]

OH and HO₂

Reactions



Rate Constants

$$k_{14} = 10^{-13} \frac{\text{cm}^3}{\# \text{ s}}$$

k_{31} : not used

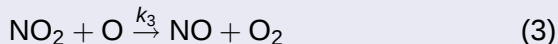
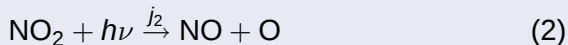
$$k_{14} = 1.7 \cdot 10^{-12} \exp(-940/T) \frac{\text{cm}^3}{\# \text{ s}}$$

$$k_{31} = 1.0 \cdot 10^{-14} \exp(-490/T) \frac{\text{cm}^3}{\# \text{ s}}$$

left: [Crutzen, 1970], right: [Sander, 2006]

Odd Nitrogen (NO and NO₂)

Reactions



Rate Constants

$$k_1 = 1.7 \cdot 10^{-12} \cdot e^{-1310/T} \frac{\text{cm}^3}{\# \text{s}} \quad k_1 = 3.0 \cdot 10^{-12} \cdot e^{-1500/T} \frac{\text{cm}^3}{\# \text{s}}$$

$$j_2 = 5 \cdot 10^{-3} \frac{1}{\text{s}} \quad j_2 = 1 \cdot 10^{-2} \frac{1}{\text{s}}$$

$$k_3 = 3.2 \cdot 10^{-11} \cdot e^{-530/T} \frac{\text{cm}^3}{\# \text{s}} \quad k_3 = 5.1 \cdot 10^{-12} \cdot e^{210/T} \frac{\text{cm}^3}{\# \text{s}}$$

left: [Crutzen, 1970], right: [Sander, 2006] & [Brasseur & Solomon]

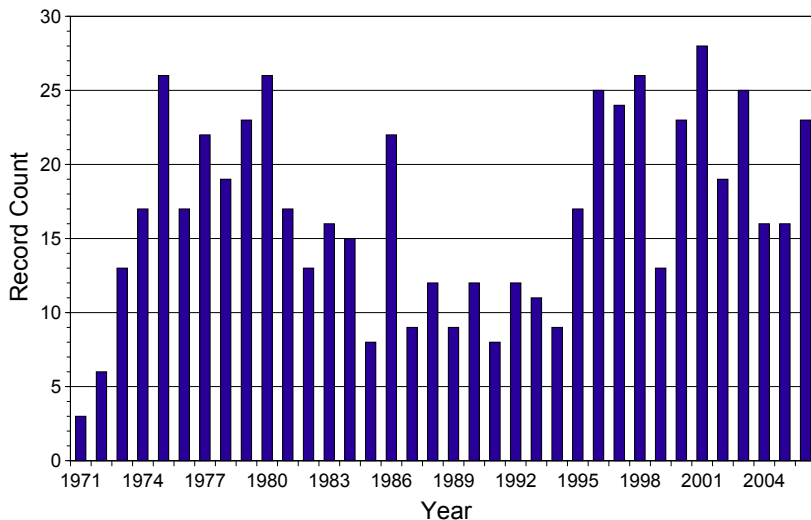
Change of Odd Oxygen (O and O₃)

Time Rate

$$\begin{aligned}
 \frac{d}{dt}[\text{O}_x] = & + \underbrace{2j_4[\text{O}_2]}_P \\
 & - \underbrace{2k_3[\text{O}][\text{NO}_2]}_{D_1} \\
 & - \underbrace{\{(k_{11}[\text{O}] + k_{14}[\text{O}_3])[\text{OH}] + k_{13}[\text{O}][\text{HO}_2]\}}_{D_2} \\
 & - \underbrace{2k_6[\text{O}][\text{O}_3]}_{D_3}
 \end{aligned} \tag{22}$$

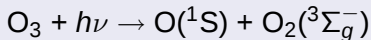
Impact

Record Count (total 600 times cited)



Discussion

- Nitrogen oxides are of great importance in ozone photochemistry
- Observations of the nitrogen oxides in the stratosphere
- Sources of N_2O
- Photodissociation products of N_2O
- Most of the NO and NO_2 is produced at very high levels, influence by solar cycle?
- What products are formed in the photolysis of ozone below 234 nm?



List of figures I



Portraits of P. J. Crutzen, M. J. Molina and F. S. Rowland

http://nobelprize.org/nobel_prizes/chemistry/laureates/1995/

Bibliography I



P. J. Crutzen

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96:320–325, 1970.



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[http://jpldataeval.jpl.nasa.gov/pdf/JPL_15_
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P. J. Crutzen

Autobiography

http:

[//nobelprize.org/nobel_prizes/chemistry/
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P. J. Crutzen

Personal Homepage

<http://www.mpch-mainz.mpg.de/~air/crutzen/>