

INTRODUCTION

Pesticides are extensively used in agriculture, gardening and a variety of other household applications. In general terms, around **45-50 %** of the active substances used are **herbicides**. They can be emitted into the atmosphere through dispersion during spraying, and also through volatilization from ground or leaf surfaces. Once in the atmosphere pesticides are distributed between the gas, particle and aqueous phases. The partitioning in different phases depends on their physicochemical properties (such as equilibrium vapour pressures, Henry's law constants) as well as on the environmental conditions (temperature, wind direction, height of cloud base).

Thiocarbamate herbicides such as Prosulfocarb (CAS: 52888-80-9, S-benzyl dipropylcarbamothioate) are used both in pre- and post-emergence in winter cereals. It can be released to the atmosphere directly while being sprayed. A vapour pressure of 6.4×10^{-3} Pa at 20 °C indicates that prosulfocarb will exist in both gas and particulate phases in the atmosphere. Studies on the gas-phase degradation of pesticides are problematic because of their low vapour pressures. One advantage of large simulation chambers, such as those at the European Photoreactor (EUPHORE), is that compounds with vapour pressures as low as 3 mPa can be introduced into the chamber in the gas-phase.

EXPERIMENTAL



EUPHORE consists of two identical half-spherical FEP (fluorine-ethene-propene) foil chambers mounted on an aluminium floor covered with FEP foil which transmits ≈ 90 % sunlight at wavelengths higher than 320 nm, dropping to 75 % transmission at the atmospheric threshold of 290 nm. The chamber used for the experiments has a volume of approximately 200 m³ and two mixing fans to ensure homogeneity of the reaction mixtures. A retractable steel housing surrounding the chamber is used to control the time of exposure to sunlight.

The present series of experiments were carried out to determine the major reaction pathways for prosulfocarb degradation in the troposphere.

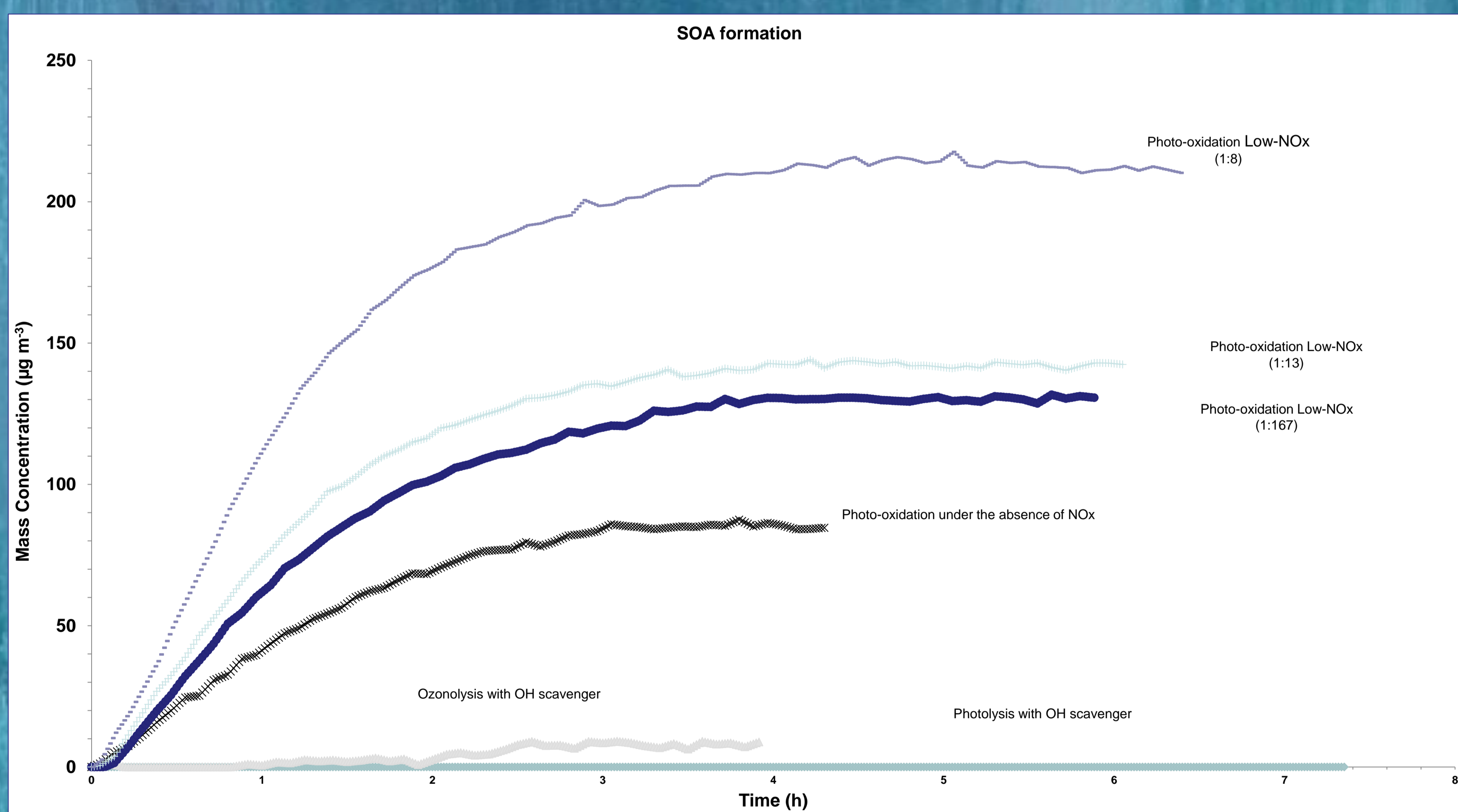
FTIR	Reactant and Products (gas-phase)	A White-type multi-reflection mirror system (path length of 553.5 m), MCT detector
Waltz Hygrometer	T and RH	Waltz TS2
Barometer	Pressure	Air-DB-VOC, Sirsa
NOx monitor	NO, NO ₂ , NOx	TAPI NO _x monitor (T200)
O ₃ monitor	O ₃	Ecotech ozone analyzer
Radiometer	Actinic Flux	Jazz
SO ₂ monitor	SO ₂	Thermo Electron monitor model 43i
(On-line)-SPME-GCMS	Reactants and products (gas-phase) (with and without on-fiber derivatization)	Agilent LTM 5975T, SPME G6501B
(Off-line)-SPME-GC-FID	Reactants (gas-phase)	Agilent 6890
(Off-line) GC-MS	Products (gas and particle phase). With and without derivatization techniques	GC-MSTRACE-DSQ II GC-MSn Thermo Electron.
(Off-line) LC MS/MS	Products (gas and particle phase)	Waters
PTRMS	Products (gas-phase)	Ionikon
SMPS	Aerosol size distribution	Model 3080 with DMA 3081 and CPC 3075

RESULTS AND DISCUSSION

Type of Experiment	Prosulfocarb (ppbV)	Cyclohexane (ppbV)	TMB (ppbV)	TME (ppbV)	H ₂ O ₂ (ppbV)	NO (ppbV)	O ₃ (ppbV)	HONO (ppbV)	RH (%)	Ratio (ppbC/ppbNO _x)	SOA Yield (%)
Prosulfocarb ozonolysis with cyclohexane as OH scavenger	116	22000	-	-	-	-	1000	-	-	-	0
Prosulfocarb relative kinetics	120	-	135	-	-	-	-	-	Cont ^(a)	-	-
Prosulfocarb relative kinetics in darkness	139	-	135	(b)	-	-	(b)	-	-	-	-
Prosulfocarb photolysis with cyclohexane as OH scavenger	83	22000	-	-	-	-	-	-	-	-	3
Photo-oxidation of prosulfocarb in the absence of NO _x (with H ₂ O ₂)	82	-	-	-	34000	-	-	-	-	-	15
Photo-oxidation of prosulfocarb in the presence of low NO _x (with H ₂ O ₂ +NO)	92	-	-	-	34000	5	-	-	-	333	18
Photo-oxidation of prosulfocarb in the presence of low NO _x (with H ₂ O ₂ +NO)	78	-	-	-	34000	10	-	-	-	167	20
Photo-oxidation of prosulfocarb in the presence of low NO _x (with H ₂ O ₂ +NO)	73	-	-	-	34000	125	-	-	-	13	25
Photo-oxidation of prosulfocarb in the presence of NO _x (with H ₂ O ₂ +NO)	43	-	-	-	34000	200	-	-	-	8	46

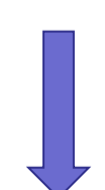
a) Cont.: Added continuously, around 2 ppb/min

b) Ozone and TME were added to generate OH in the darkness



Conclusions:

- In the gas phase prosulfocarb would have a relatively short lifetime \rightarrow mainly due to reaction with OH radicals.



- Undergo short or medium-range transport (during night hours –no photochemical activity- depending on the wind speed, could be transported medium or large distances)
- Heterogeneous losses could be a significant removal source.
- Main degradation products for the reaction of prosulfocarb and OH radicals: benzaldehyde, benzoic acid, S-benzylformyl(propyl)carbamothioate, and S-benzylpropanoyl(propyl)carbamothioate \rightarrow relevant aerosol precursor, with aerosol yields of 14-46% or greater under high NO_x conditions.

PHOTOLYSTS UNDER SUNLIGHT CONDITIONS

$$J_{\text{prosulfocarb}} < 1.7 \times 10^{-4} \text{ s}^{-1} \text{ at } 288 \pm 10 \text{ K}$$

Lifetime ($\tau=1/J$) >10 h in autumn, at 288 ± 10 K and 40° latitude. Two photolysis compounds detected at trace level.

REACTION WITH OZONE

$$k_{\text{O}_3}(\text{prosulfocarb}) < 1.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

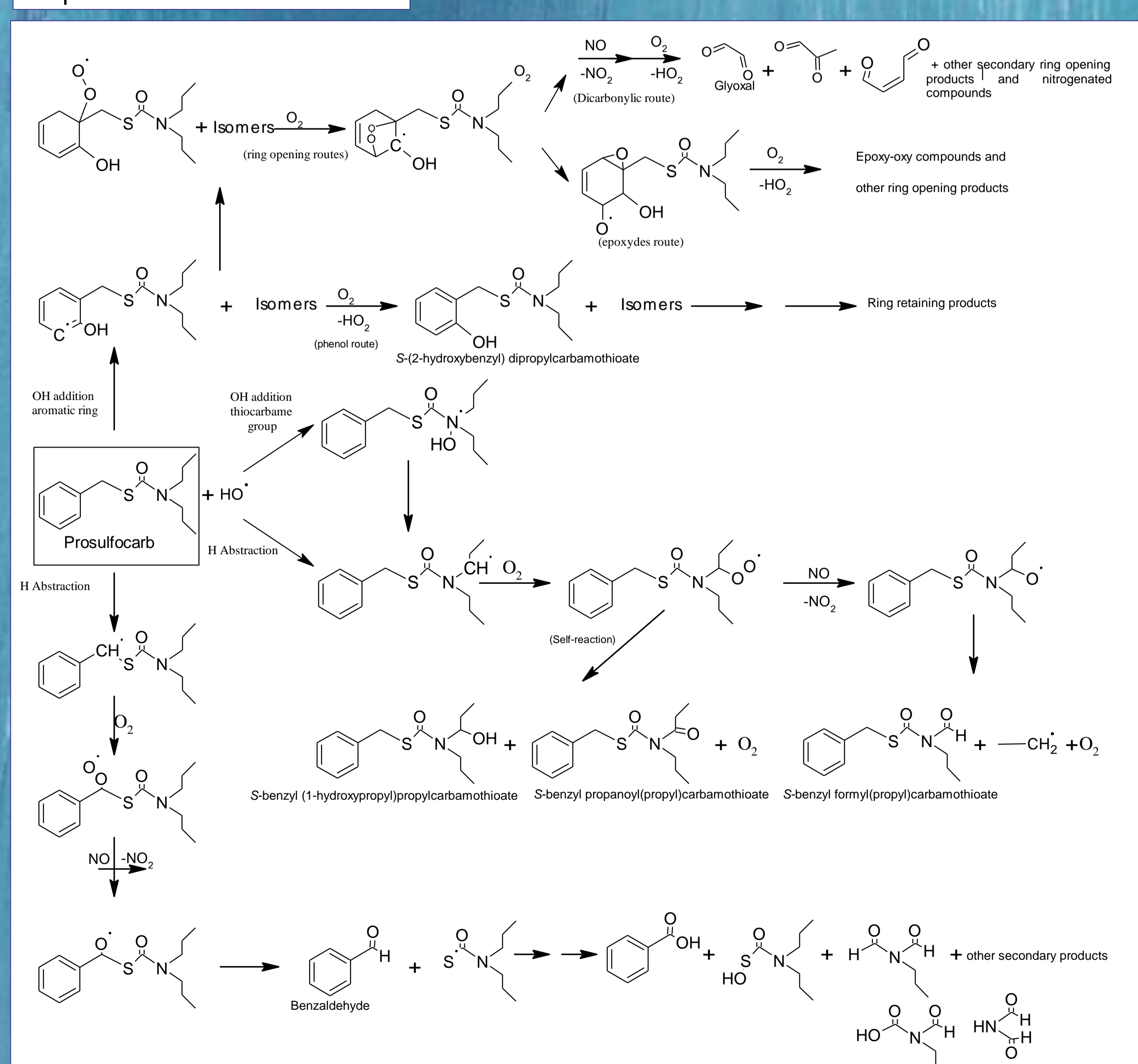
Lifetime ($\tau_{\text{O}_3}=1/k_{\text{O}_3}[\text{O}_3]$) >13 days at $[\text{O}_3]_{\text{average}} = 7 \times 10^{11} \text{ molecule cm}^{-3}$
No reaction products detected.

REACTION WITH HYDROXYL RADICALS

$$k_{\text{OH}}(\text{prosulfocarb}) = 2.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Lifetime ($\tau_{\text{OH}}=1/k_{\text{OH}}[\text{OH}]$) = 6.2 hours at $[\text{OH}]_{\text{average}} = 1.56 \times 10^6 \text{ radical cm}^{-3}$
High variety of products detected

Proposed reaction mechanism:



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