TNA User Report

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Project title	Atmospheric Degradation of a Series of Epoxy Compounds
Name of the accessed chamber	HELIOS
Number of users in the project	2
Project objectives (max 100 words)	Epoxy compounds are cyclic oxygenated hydrocarbons emitted into the atmosphere solely from anthropogenic sources. They are important for chemical industry worldwide due to their ability to polymerize. However, the information on the gas-phase degradation of epoxides and the subsequent implication for environmental issues is scarce or missing. This project aims to explore in depth the gas-phase degradation of selected epoxides toward a comprehensive evaluation of their atmospheric fate. HELIOS was chosen due to the possibility of using daylight and an array of instrumentation complementary to those available in the home laboratory. Achieving training on the complementary techniques is also targeted.
Description of work (max 100 words):	The reactions of 1,2-epoxybutane, 1,2-epoxyhexane and cyclohexene oxide with chlorine atoms and OH radicals were studied under mechanistic aspects. All measurements were conducted at 296 ±2 K and at ambient pressure (P = 760 Torr). The product formation was analysed via IR- and mass spectrometry as complementary techniques. OH radicals and Cl atoms were produced via photolysis of methyl nitrite and oxalyl chloride, respectively. Additionally, the formation of particles in the system was monitored via SMPS.

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[1] UNI= University and Other Higher Education Organisation.
[2] PGR= Post graduate; RES= Researcher.

Trans-National Access (TNA) Scientific Report

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Name of the PI: Peter Wiesen
Chamber name and location: HELIOS, CNRS/ICARE Orleans
Campaign name and period: EUROCHAMP 2020, Atmospheric Degradation of a Series of Epoxy Compounds, July 13th – August 3rd, 2019

Introduction and motivation

Epoxy compounds (EpCo) are cyclic oxygenated hydrocarbons emitted worldwide in the atmosphere from anthropogenic sources. They are an important and valuable class of raw materials and intermediates for chemical industry. Through polymerization EpCO yield production of homo- and copolymers such as polyethers, polyols and polycarbonates. Cycloaliphatic epoxides (e.g. cyclohexene oxide) are among the major types of epoxy resins utilized in coatings industry and have been extensively used as binders for cationic ultraviolet light cured overprint varnishes, inks, non-metal substrate (wood, paper and plastic) coatings, and electrical/electronic coatings.

Although a large variety of EpCo are released accidentally in the atmosphere, the information on their gas-phase chemistry is limited and available only for few of them. It is known that some EpCo are harmful when inhaled and it is possible that the products of their atmospheric degradation are as well. Moreover, former studies indicate that EpCo are involved in the growth and, possibly, in the formation of secondary organic aerosols (SOA, Gao et al. 2004, Lin et al. 2013).

Through the present work we intend to fill some of the gaps associated with the atmospheric degradation of EpCo in order to be able to evaluate more comprehensively their role in the atmosphere.

Scientific objectives

The main objective of this study is to explore in depth the reaction mechanism and reactivity associated with the gas-phase degradation of epoxides by OH radicals and Chlorine atoms.

For this, based on preliminary data achieved in our home laboratory in Wuppertal, we selected the following epoxy compounds: 1,2-epoxybutane, 1,2-epoxyhexane and cyclohexene oxide as model substances for this study.

For these compounds there are no other data (such as theoretical or experimental studies of their reactivity trends or detailed product analyses) available from which the potential impact of this compounds upon the atmosphere could be derived.

Reason for choosing the HELIOS simulation chamber. Method and experimental set-up

The majority of the measurements were carried out in the hemispheric HELIOS atmospheric simulation chamber. By comparison with the home laboratory, the HELIOS chamber offers the possibility of using real solar light in simulation experiments. With a total volume of 90 m^3 and a surface to volume ratio of 1.2 m^{-1}, Helios is protected from intense weather phenomena via a

specially designed movable dark-housing and it is made of a 250 µm Teflon FEP film that allows >90 % of the solar radiation to enter into the chamber.
A variety of instrumentation is available to be connected to HELIOS such as 300 m of optical path on-line FTIR, PTR/ToF-MS (Ionicon 8000), Aerodyne ToF-CIMS, ATD-GC-MS, UHPLC, IC, SMPS, LOPAP HONO analyzer, Aerolaser 4021 HCHO analyzer, Spectroradiometer and monitors of O_3, and NOx (NO + NO_2).
This activity did target training of a postgraduate student on using new techniques in investigating atmospheric chemistry processes.

In the present study, the FTIR and PTR/ToF-MS were primarily used to monitor the reactants and products in the gas phase. An O_3 monitor was connected whenever needed. In addition, the particle formation was monitored using a CPC-SMPS system.
A complete characterization of the SOA fraction formed in the experiments is not foreseen due to the tight time schedule.
All measurements were conducted at 296 ±2 K and at ambient pressure (P = 760 Torr).

The gas reactants were admitted into the photoreactor via calibrated buffer volumes, while liquids were directly injected via titrated syringes. For compounds of lower volatility were used bubblers ensuring that the vapors were flushed into the chamber carried by a pure air flow. SF6 was used as nonreactive marker in all determinations in order to measure dilution and other first-order losses of the reactants, e. g., wall-loss.
Cl atoms were generated through the photolysis of oxalyl chloride $(ClCO)_2$:

$$(ClCO)_2 + h\upsilon \rightarrow 2Cl + 2CO$$

OH atoms were produced by photolysis of methyl nitrite (CH_3ONO) in the presence of NO in air:

$$CH_3ONO + h\upsilon \rightarrow CH_3O + NO$$
$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$
$$HO_2 + NO \rightarrow OH + NO_2$$

The CH_3ONO was synthesized within the reaction of $NaNO_2$ with CH_3OH and kept under in the liquid nitrogen.
Before each experiment, the chamber was cleaned by flushing pure air (800 L per min) for at least 12 hours.

The following experiments were performed over three weeks:

Week	*Compound*	*Experiment*	*No. of experiments*
1	1,2- epoxybutane	Product study towards Cl atoms/NO	1
		Product study towards OH radicals	2
		Product study towards OH radicals/ SOA formation	2
2	1,2 –epoxyhexane	Product study towards Cl atoms/NO	1
		Product study towards OH radicals	2
		Product study towards OH radicals/ SOA formation	2
3	cyclohexene oxide	Product study towards Cl atoms/NO	1
		Product study towards OH radicals	2
		Product study towards OH radicals/ SOA formation	2

Preliminary results and conclusions

With the assistance of the HELIOS research team, the experiments were performed as scheduled and valuable practical knowledge in operating a different set of instruments were achieved.
Although the evaluation of the results is not complete, preliminary results are promising confirming the formation of some of the products expected from theoretical considerations.

Outcome and future studies

The data emerging from this activity does contribute to the PhD thesis of Carmen Tovar. This is schedule for defense during the first half of 2020.
The final results will be included in a common publication with the host group, which is scheduled for submission in the late 2020.

References

Gao, S.; Ng. Nga L., Keywood, M.; Varutbangkul, V.; Bahreini, R.; Nenes, A.; He, J.; Yoo, K.; Beauchamp, J.; Hodyss, R.; Flagan, R.; Seinfeld, J. Environ.Sci.Technol. 2004, 38, 6582-89. doi.org/10.1021/es049125k

Lin Y.H.; Zhang H.; Pye H.O.; Zhang Z.; Marth W. J.; Park S.; Arashiro M.; Cui T.; Budisulistiorini S.H.; Sexton K. G.; Vizuete W.; Xie Y.; Luecken D. J.; Piletic I. R.; Edney E. O.; Bartolotti L. J.; Gold A.; Surratt J. D. Proc Natl Acad Sci U S A. 2013, 110(17), 6718-23. doi: 10.1073/pnas.1221150110