Chapter 6

CONCLUSIONS

The preceding chapters of this thesis, along with the following appendices, contribute to the substantial recent progress in our understanding of the HO_2-dominated pathway of isoprene oxidation, and how that sub-mechanism fits into the broader contexts of both isoprene oxidation in general and the chemistry of the atmosphere as a whole. In the eight years since the publication of IEPOX's discovery (Paulot *et al.*, 2009b), a wealth of research has been conducted into its possible fates and reactive pathways, aided by the development of synthetic pathways for the production of four IEPOX isomers (Zhang *et al.*, 2012). The rates and products of its reaction with OH have been quantified, first by Jacobs *et al.* (2013) and then in the studies described in Chapters 2 and 3; subsequent experiments detailed in Chapter 3 also explored the chemistry of those products. Its contribution to SOA was first investigated in the laboratory by Lin *et al.* (2012) and Nguyen *et al.* (2014a) (Chapter 5), and many ensuing studies have contributed to this line of enquiry by examining particle phase reaction probabilities (Riedel *et al.*, 2015), the effects of aerosol acidity (Gaston *et al.*, 2014; Liu *et al.*, 2015; Wong *et al.*, 2015) and organic coatings (Riva *et al.*, 2016a) on IEPOX uptake, and the chemical composition (D'Ambro *et al.*, 2017a; Riva *et al.*, 2016b) and light-absorbing properties (Lin *et al.*, 2014) of that IEPOX-derived SOA. Additional studies of minor chemical pathways, such as dry deposition (Nguyen *et al.*, 2015a) and low-yield products of ISOPOOH chemistry (Berndt *et al.*, 2016; D'Ambro *et al.*, 2017b; Krechmer *et al.*, 2015; Liu *et al.*, 2016) have further amplified our understanding of isoprene's HO_2-dominated oxidation mechanism. Finally, as described briefly in Chapter 4, the results of these studies and others are now being incorporated into chemical models and used to investigate the importance of these newly explored oxidation pathways, as well as their effects on oxidant budgets, SOA formation, and other variables of interest in regional and global contexts (Marais *et al.*, 2016; Travis *et al.*, 2016).

As a result of the work in this thesis and the related studies mentioned above, the sinks of IEPOX have largely been constrained. Despite its myriad dependences on OH concentrations, the turbulence and depth of the mixing layer, and particle surface area and composition, the initial atmospheric fate of IEPOX can now be parameterized and modeled. Results from a number of such simple models are listed in Table 6.1, including some based on measured ambient conditions. Further validation of IEPOX oxidation, uptake, and deposition parameterizations with field measurements will enable their implementation in more complex and broad-scale models.

Despite this recent progress, some aspects of the HO_2 dominated isoprene mechanism remain poorly constrained, which present promising avenues for further research. First, although many initial particle-phase products from the reactive uptake of IEPOX have been characterized, the potential reactivity and atmospheric fate of IEPOX-derived SOA is largely unknown. Aerosol aging encompasses a complex set of processes (including condensed-phase reactions, heterogeneous chemistry, photolysis, cloud processing, and others) that can cause changes in SOA chemical composition (George *et al.*, 2007; Molina *et al.*, 2004) and optical properties (Sareen *et al.*, 2013) and can even form volatile products that return to the gas phase (D'Ambro *et al.*, 2017a; Malecha and Nizkorodov, 2016; McNeill *et al.*, 2008). Preliminary results from the Seinfeld and McNeill laboratories suggest that exposure of IEPOX-derived SOA to gas-phase OH can cause rapid fragmentation of particle-phase organic species, leading to the volatilization of small acids and other compounds. If, as would thus be expected, these aging processes and their gas-phase products affect the lifetime of IEPOX-derived SOA and its overall loading, ozone formation, or oxidant cycling, then quantifying their effects they would be of vital importance to accurately describing the role of the HO_2-dominated isoprene oxidation pathway in the atmosphere.

Another auspicious field of future research regards unexplored product channels of the HO_2-dominated oxidation mechanism, including both later-generation chemistry and minor products from early generations that may have previously escaped detection. Chapter 3 identified stable oxidation products up to the fourth generation beyond isoprene, and observed that most compounds at that stage had fragmented to contain four or fewer carbon atoms, making them less likely to contribute to SOA; still, the dominant products are formed in such high abudnance (*e.g.*, the fourth-generation C_4 hydroxydicarbonyls are produced in excess of 50 Tg y^{-1} from isoprene oxidation) that their subsequent chemistry could have significant effects on local oxidant levels, radical cycling, and ozone formation. Additionally, new classes of highly oxidized compounds have recently been identified as potential minor products from the oxidation of ISOPOOH, including dihydroxy-dihydroperoxides and dihydroxy-hydroperoxy-epoxides (Berndt *et al.*, 2016; D'Ambro *et al.*, 2017b; Krechmer *et al.*,

		pathway contributions (%)		
citation	conditions	+ OH (gas phase)	particle uptake	dry deposition
Worton *et al.* (2013)	ambient: Sierra Nevada, CA, summer	52	<1	48
Gaston *et al.* (2014)	[OH]~10^6 molec cm^{-3}, ~100 $\mu m^2 cm^{-3}$ $(NH_4)_2SO_4$ particles	57	1	42
Gaston *et al.* (2014)	[OH]~10^6 molec cm^{-3}, ~100 $\mu m^2 cm^{-3}$ $(NH_4)HSO_4$ particles	30	48	22
Nguyen *et al.* (2015a)	low or non-acidic particle limit	-	-	≤45
Bates *et al.* (2016)	[OH]~2.5×10^6 molec cm^{-3}, ~200 $\mu m^2 cm^{-3}$ pH 3 particles	44	37	19
Hu *et al.* (2016)	ambient: Centreville, AL, summer	9	75	16

Table 6.1: Estimates of the relative contributions of reaction with OH, particle uptake, and deposition as pathways for the loss of gas phase IEPOX under various atmospheric conditions.

2015; Liu *et al.*, 2016). Despite their low yields, these products could contribute a substantial portion of isoprene-derived SOA under HO_2-dominated conditions due to their low volatility. These compounds are difficult to measure because of their rapid losses to chamber walls and instrumental surfaces, but new methods are now being employed to detect them directly or through their contribution to SOA. Further constraining the yields and uptake of these highly oxidized products is necessary to better understand and model SOA formation from the HO_2-dominated isoprene oxidation pathway.

Finally, the improved representation of isoprene reaction mechanisms in chemical transport models, for the sake of both comparison with field measurements and investigating the broader effects of isoprene oxidation, presents another promising avenue for further research. Notwithstanding from the comprehensive treatment of isoprene oxidation in Chapter 4, recent developments in isoprene chemistry have only been incorporated into global models on an *ad hoc* basis (*e.g.* in Chapter 3 and Appendices B, D, and G). Despite many recent improvements, chemical transport models still fail to accurately represent regional and global concentrations of isoprene-derived VOCs (Travis *et al.* (2016) and Appendix 7) as well as trace gases of broader importance such as OH (Turner *et al.*, 2017; Voulgarakis *et al.*, 2013) and ozone (Apel *et al.*, 2012; Parrish *et al.*, 2014; Whalley *et al.*, 2010). This thesis has demonstrated the importance of HO_2-dominated isoprene chemistry to such trace gas budgets across wide swaths of the globe; it is imperative that models incorporate accurate representations of this chemistry in order to determine isoprene's effects on air quality and climate, and to look at how those effects may change in the future. SOA, in particular, is currently only given cursory treatment in most chemical transport models. Given its high and uncertain importance to climate forcing (Pachauri *et al.*, 2014), the potential for significant changes in future SOA loading (Lin *et al.*, 2016), and the major contribution of HO_2-dominated isoprene chemistry to global SOA budgets, improving parameterizations of SOA and the chemistry of its precursors in models will be a prominent direction for further research.

The importance of isoprene to the chemistry of the troposphere can hardly be overstated; its high emissions and reactivity mean that even minor channels in its oxidation mechanism can play outsized roles in local atmospheric chemistry, and major oxidation channels, such as the HO_2-dominated pathway, can effectively set oxidant cycling, ozone production, and SOA formation rates across broad swaths of the globe. Comprehending this mechanism is thus crucial to determining the role isoprene plays in affecting air quality and climate, and how that role may change over time. This thesis has presented a small but important step toward that comprehension, and will hopefully inform future studies that can bring us even closer to that goal.