

Molecular corridors represent the multiphase chemical evolution of secondary organic aerosol

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The dominant component of atmospheric organic aerosol is that derived from the oxidation of volatile organic compounds (VOCs), so-called secondary organic aerosol (SOA). SOA consists of a multitude of organic compounds, only a small fraction of which has historically been identified. Formation and evolution of SOA is a complex process involving coupled chemical reaction and mass transport in the gas and particle phases. Current SOA models do not embody the full spectrum of reaction and transport processes nor do they identify the dominant rate-limiting steps in SOA formation. The recent advent of soft ionization mass spectrometry methods now facilitates a more complete molecular identification of SOA than heretofore possible. Based on such novel measurements, we show here that the chemical evolution of SOA from a variety of VOC precursors adheres to characteristic “molecular corridors” with a tight inverse correlation between volatility and molar mass. Sequential and parallel reaction oxidation and dimerization pathways progress along these corridors through characteristic regimes of reaction-, diffusion-, or accommodation-limited multiphase chemical kinetics that can be classified according to reaction location, degree of saturation, and extent of heterogeneity of gas and particle phases. These molecular corridors constrain the properties of unidentified products and reaction pathways and rates of SOA evolution, thereby facilitating the further development of aerosol models for air quality and climate.