

Chapter 5

Summary and outlook

5.1 New signatures, new reactions

Presently, the large enrichment in $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ we found in the stratospheric polar vortex is still unexplained. The laboratory photochemical experiments we reported in Chapter 2 seem to rule out $\text{O}(^1D) + \text{CO}_2$ isotope exchange; stratospheric $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ should get more depleted with increasing extent of isotope exchange, not enriched, and we observed this trend as a decrease in Δ_{47} in field samples from the mid-latitude stratosphere. What, then, could enrich $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ in the polar vortex, and what might we be able to learn from future studies?

We suggested in Chapter 2 that fast low-temperature isotopic equilibration of CO₂ on stratospheric particles (e.g., PSCs) could be responsible for the high Δ_{47} values in the polar vortex. Our initial tests of the PSC-isotope-equilibration hypothesis suggested that isotopic equilibration on certain HNO₃ ices and H₂SO₄:HNO₃:H₂O mixtures is slow, and is therefore unlikely to produce $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ enrichments on timescales that would be consistent with our polar vortex data. The CO₂ isotopic equilibration rate, however, could be sensitive to particle structure and composition. PSCs and cirrus clouds form under similar conditions, but they can differ in bulk and surface composition [Zondlo *et al.*, 2000]; the structure, physics, and chemistry of these particles are still not understood [Dash *et al.*, 2006; Lowe and MacKenzie, 2008], so the role of CO₂ isotopic equilibration on ice particle surfaces remains uncertain. Future laboratory work on CO₂-ice surface interactions may shed light on the structure and composition of these and other atmospherically important particles.

We also identified three new reactions, O₂ + CO₂ and O(³P) + CO₂ isotope exchange and O(³P) + CO₂ → O₂ + CO, in our crossed-molecular-beam experiments. Because of the ≈160 kcal mol⁻¹ reaction barrier for O₂ + CO₂ isotope exchange, and the ≈75 kcal mol⁻¹ barrier for O(³P) + CO₂ → O₂ + CO, they are unlikely to be important in the stratosphere. O(³P) + CO₂, in contrast, has a reaction barrier (≈ 25 kcal mol⁻¹) that is atmospherically accessible, in principle.

5.2 Potential atmospheric importance of O(³P) + CO₂

The laboratory observation of O(³P) + CO₂ isotope exchange at hyperthermal energies may have implications for modeling the oxygen isotope cycling in the middle and upper atmosphere because current models do not include O(³P) + CO₂ reactions explicitly [Liang *et al.*, 2007, 2008; Thiemens *et al.*, 1995; Yung *et al.*, 1991, 1997]. Here, I suggest that O(³P) + CO₂ reactions in the upper atmosphere could affect the oxygen isotope distribution in CO₂. The O(³P) + CO₂ isotope exchange reaction could yield isotope effects qualitatively different from those in the O(¹D) + CO₂ reaction because its mechanism is direct, unlike the mechanism involving a long-lived CO₃* intermediate for the O(¹D) + CO₂ reaction [Chen *et al.*, 2009; Perri *et al.*, 2003, 2004]. Instead, like the O₃* complex in the O(³P) + O₂ isotope exchange reaction [Van Wyngarden *et al.*, 2007], the CO₃* reaction complex formed from O(³P) + CO₂ does not live long enough for its energy to randomize; thus, dynamical isotope effects are likely to be important to its isotope-specific branching fractions. These types of non-statistical isotope effects are believed to be partly responsible for “anomalous” formation rates of stable O₃ from the O₃* complex for different isotopologues [Babikov *et al.*, 2003; Gao and Marcus, 2001; Schinke *et al.*, 2006]. Due to limitations in our apparatus, however, we were unable to investigate the O(³P) + CO₂ isotope exchange dynamics near the predicted reaction threshold, which is more relevant to the atmosphere. Our reactive trajectories at $E_{\text{coll}} = 1.0$ and 1.5 eV (23.0 and 34.6 kcal mol⁻¹, respectively), however, suggest that isotope exchange is still direct near the calculated reaction barrier.

The overall importance of the O(³P) + CO₂ isotope exchange reaction to reactive oxygen cycling in the atmosphere, however, depends on (1) the reaction’s excitation function

and (2) the proportion of O(³P) in the atmosphere with sufficient translational energy to surmount the reaction barrier. In the absence of experimental data, high-level variational quantum calculations can assign an upper limit to the TS1 barrier. The CCSD(T)/aug-cc-pVTZ energy for TS1 (25 kcal mol⁻¹) reported in this work implies that relative velocities of ≥ 3 km s⁻¹ in the ground-state reactants will be required to open the isotope exchange channel; ozone photolysis in the Hartley band (220 – 310 nm) and at shorter wavelengths yields O(³P) + O₂(³Σ_g⁻) photofragments having a total translational energy in excess of 25 kcal mol⁻¹ and as high as 100 kcal mol⁻¹ [Fairchild *et al.*, 1978; Kinugawa *et al.*, 1990; Shamsuddin *et al.*, 1994; Stranges *et al.*, 1995; Syage, 1995; Takahashi *et al.*, 1998]. Our preliminary hard-sphere collision modeling (see Appendix 2.D) using cross-sections for the velocity relaxation of O(¹D) by N₂ [Matsumi and Chowdhury, 1996; Matsumi *et al.*, 1994b] suggests that the size of the reactive O(³P) reservoir could be as high as several percent that of O(¹D). Future theoretical and experimental studies can elucidate the shape of the reaction's excitation function, which is needed before an appropriate simulation can be constructed. Finally, we note that during our laboratory study of the O₂/O₃/CO₂ photochemical system using a mercury lamp as an actinic light source (185 and 254 nm), we observed deviations from modeled results at long irradiation times ($t \sim$ days; see Figure 2.8); a minor O(³P) + CO₂ channel could address part of this discrepancy, as well as some of the disagreements between earlier studies [Chakraborty and Bhattacharya, 2003; Johnston *et al.*, 2000; Shaheen *et al.*, 2007; Wen and Thiemens, 1993]. The yield of hyperthermal O(³P) during O₃ photolysis depends on wavelength [Stranges *et al.*, 1995; Takahashi *et al.*, 1998], however, so this hypothesis awaits further testing with systematic studies of the O₂/O₃/CO₂ photochemical system.

Claims of hyperthermal O(³P) + CO₂ chemistry in the atmosphere based on laboratory data must be met with some skepticism, however. Both N₂ and O₂ are efficient energy quenchers for even the most reactive atmospheric species, and the steady-state population of fast-moving O(³P) will be determined largely by its translational relaxation rate in air. In addition, thermal averaging collapses most reaction rates towards the chemical kinetic limit, so any atmospheric signature of the O(³P) + CO₂ reaction will be difficult to identify

unless the associated isotope effect is large and unique. Previously published reports of hyperthermal chemistry in the atmosphere based only on laboratory evidence have been controversial due to the lack of an unequivocal signature in the field data [*Li et al.*, 2008; *Miller et al.*, 1994]. The stratospheric ¹⁶O¹³C¹⁸O enrichment reported in Chapter 2 is a clear signature of *some* heretofore unknown process, but definitive tests of the hyperthermal O(³P) + CO₂ isotope-exchange hypothesis will have to take the form of well-characterized, rigorously modeled bulk photochemical experiments involving O₃ and CO₂.