

Interactive comment on “Investigations of the photochemical isotope equilibrium between O₂, CO₂ and O₃” by R. Shaheen et al.

R. Shaheen et al.

Received and published: 27 November 2006

We thank Carl Brenninkmeijer for his thoughtful comments and suggestions. Before we discuss the five points raised in his report in some detail, we would like to specify his statement that “in Table 2, the slope is based on single points, and not the evolution of a mixture in time”.

The data from *our new experiments* reported in this paper, lines 1-6 of Table 2, report slopes that were determined from time evolutions and not from the equilibrium point only. This also holds for the measurements of Chakraborty and Bhattacharya (2003) listed in lines 16-18. The situation is different, however, for the data presented in lines 7-15 (Johnston et al (2000) and Wen & Thiemens (1993)). For those experiments no

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

data for the time evolution is available and only the initial and final isotope compositions were used to determine the observed slopes. These slope values are therefore based on two points rather than on only one data point.

1. Ozone Content

Due to the remaining vapour pressure of O_3 at liquid nitrogen temperature, O_3 cannot be trapped quantitatively in a liquid nitrogen cooled trap, where the vapour pressure is around 0.2 Pa. Therefore, we unfortunately have not been able to reliably quantify O_3 concentrations in our experiments and have only two rather qualitative remarks. 1) In most of the experiments we observed a slight blue colour in the CO_2 trap, which is indicative of O_3 . 2) The isotope mass balance, i.e., $c(CO_2)_i \delta(CO_2)_i + c(O_2)_i \delta(O_2)_i - c(CO_2)_f \delta(CO_2)_f - c(O_2)_f \delta(O_2)_f$, where c denotes the concentration, δ the delta value and the indices i and f the initial and final values, was in the case of the oxygen dominated mixture ($\rho \sim 120$) closed within 0.25 per mil \pm 0.35 per mil (2σ). Given that O_3 is about 100 per mil enriched relative to O_2 , this indicates that O_3 levels were at most 0.25% of O_2 levels, corresponding to a partial pressure of (60 \pm 80) Pa

2. Effect of Ni

The effect of the decomposition of O_3 on a Ni surface was investigated in detail in [Johnston *et al.*, 2000]. In that study the authors indeed determined a slight enrichment in CO_2 from the decomposition of O_3 on Ni, which amounted to 2-3 per mil for $\delta^{17}O$ and $\delta^{18}O$. However, in those test experiments the amount of O_3 exceeded that of CO_2 , which is due to the high O_2/CO_2 ratios applied for some experiments in that study. We have used lower O_2/CO_2 ratios, and based on the O_3/O_2 ratio of $<1\%$ (see above) we expect that the O_3/CO_2 ratio was about one order of magnitude lower than that tested in [Johnston *et al.*, 2000]. Therefore, the effect of Ni is most likely negligible for our experiments.

3. Mass independent fractionation in $O(^1D)+CO_2$

We have indeed reported one experimental result that is a strong indication for a fractionation in the $O(^1D)+CO_2$ exchange process, namely the ρ dependence of the experimental results. The equilibrium enrichments change in a non mass dependent fashion with ρ . According to our understanding of the ozone isotope enrichments, this cannot originate from O_3 and thus it indicates non mass dependent fractionation in the exchange process itself. This is explained on page 7883, top, and we will clarify this point further in the revised version.

4. Additional figure

We have incorporated an additional figure in the revised manuscript that shows our results translated to the stratospheric situation.

5. Effect of isotope composition

We are thankful for the comment on our statement that the isotope composition of CO_2 at photochemical isotope equilibrium with oxygen and ozone is independent of the initial isotopic composition of CO_2 and O_2 used. The question of the referee was the incentive for us to elaborate a bit on this statement.

First, we note that the case mentioned by the referee, namely the hypothetical case of CO_2 and O_2 without ^{18}O , may itself be a bit confusing, because in this case one would not need to carry out isotope exchange experiments in the first place.

However, we did not discuss in the original manuscript that our conclusion only holds for isotope mixtures of near-natural heavy isotope abundance (which includes the normal or anomalous enrichments of the order of few hundred per mil as used in our paper). The limit to the statement is that the isotope chemistry should be determined by singly substituted species only, e.g., ^{18}O should only be produced by singly substituted O_3 . In strongly enriched mixtures, a departure from this behavior is expected. For example, in 50:50 mixtures of ^{16}O and ^{18}O , the isotopomer enrichment of equilibrated $^{50}O_3$ and $^{52}O_3$ is almost equal, i.e., $E(50) = E(52) \sim 10\%$ and $E(54) \sim E(48) = 0\%$ (Mauersberger

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

et al. 1993 (Geophys. Res. Lett. 20, 1031), Janssen et al. 2003 (Chem. Phys. Lett. 367, 34)). Considering only isotope effects due to the abundance of O₃ molecules, ⁴⁸O₃ and ⁵⁴O₃ produce O(¹D) and Q(¹D) (where Q = ¹⁸O) at equal amounts. ⁵⁰O₃ and ⁵²O₃ do the same. Therefore, the expected Q/O ratio is 1 and Q(¹D) will not be enriched. This is different from natural oxygen mixtures, where Q(¹D) comes from ⁵⁰O₃ only. Since that is enriched, Q(¹D) will be too.

In addition – though likely smaller in magnitude – there are even more factors that could cause a dependence on the initial isotopic composition when changing the isotope composition of the reactants from slightly to heavily enriched: isotope dependent quenching efficiencies of O(¹D) and CO₃^{*}, ozone isotopomer dependent photolysis rates and mass dependent rates of the O(¹D) + CO₂ reaction, which would include reactions with CQ₂, for example.

We have included this discussion in the revised version of our manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7869, 2006.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)