

Interactive comment on “Impact of organic nitrates on urban ozone production” by D. K. Farmer et al.

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The paper looks at the role of branching between formation of hydroperoxy radicals (HO₂) and organic nitrates from reactions of organic peroxy radicals (RO₂) with nitrogen oxide (NO) for atmospheric ozone formation. The main merit of the paper is that the authors derive a simple function that allows estimates of ozone production rate as function of VOC reactivity and NO_x concentration for given values of the branching ratio (α) and HO_x production rates and the use of this dependence to evaluate the importance of the branching ratio for ozone production rates. Furthermore, they use this relation to discuss results from a field study and present an interesting, although somewhat hypothetical example for an increase in ozone production upon reduction of VOC reactivity if a decrease in VOC reactivity is combined with decrease in aver-

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age branching ratio. Overall this is an interesting and relevant contribution towards a better understanding of the details of atmospheric VOC-NO_x chemistry using simple calculation tools (in contrast to complex numerical model simulations). I agree in principle with the concept that the branching ratio is something that should be considered in VOC reduction strategies (similar to many other specific properties VOC) but I have some minor concerns which may be sorted into three categories, (i) clarification of uncertainties in the predictions and validity of assumptions for different ranges of VOC reactivity and NO_x concentrations, (ii) relevance of the hypothetical connection between reduction in VOC reactivity and branching ratio for the real world, and (iii) the connection of predictions from this study with emission rates (“emission controls”).

i) Uncertainty and Range of Validity for Predictions of Ozone Formation Rates

It is mentioned that “high NO_x” (specifically conditions where all RO₂ radicals reacts with NO only) is one of the requirements used to derive the algebraic solutions for calculation of the OH-radical concentration (Equations 8-12). However, it is not obvious from Figures 1 and 2 for which part of the presented results these conditions are met. Figure 1 includes scenarios with 0.1 ppb of NO_x and VOC reactivity up to 20 s⁻¹. Under these conditions bias introduced by the simplification that all RO_x and HO_x react only with NO may be substantial. In any case, even if the bias may be small, the impact of changes in branching ratio α on ozone production rates often also is small. Another potential problem resulting in uncertainty or bias is the NO over NO₂ ratio used to convert NO_x concentrations into NO and NO₂ concentrations. Figure 1 and 2 use NO_x concentrations as axis, but equations 10 and 11 explicitly use NO and NO₂ concentrations. This is a non-trivial problem for an algebraic solution since the NO over NO₂ ratio will depend on HO₂ and RO₂ concentrations as well as ozone levels, which in turn depend on VOC reactivity, NO_x, OH radical concentration and other factors. A detailed explanation how this problem was solved is needed.

ii) Relation between VOC Reactivity and Branching Ratio α

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The abstract states “Current thinking treats NO_x and organics as independent variables that limit O₃ production depending on the NO_x to organic ratio; in this paradigm, reducing organics either has no effect or reduces O₃. We describe a theoretical counterexample where NO_x and organics are strongly coupled and reducing organics increases O₃ production”. Later in the introduction it is mentioned that “Here, we demonstrate that the production of organic nitrates (molecules of the form RONO₂) during oxidation of organics confounds the usual assumption that organics and NO_x are independent variables that can be considered separately in ozone control strategies, and show that in some cases organic reductions that are presumed in the standard conceptual model to be effective at reducing ozone can be counterproductive and result in ozone increases.” While I agree that there is complex feedback between NO_x, VOC, ozone, and so on, these statements may create some confusion about what is actually done in the paper. The presented solution for determining ozone production rates uses a set of equations (9-12) to approximate the OH-radical concentration (which then is used to create an approximation for ozone production rates) for a given set of variables and parameters, namely reaction rate constants, VOC reactivity, NO and NO₂ concentrations, production rate of HO_x, and branching ratio α . Mathematically speaking in these equations the variables and parameters are independent of each other and the solution does not consider feedback between these variables and parameters. In other words, the authors introduce the average branching ratio as an additional parameter (in addition to the total VOC reactivity) for describing the properties of atmospheric VOC. In the next step the authors use the algebraic solution to study the combined impact of changes in VOC reactivity and NO_x concentration for different branching ratios α . Finally they consider a hypothetical case where the branching ratio α depends in a specific way on VOC reactivity. This example is chosen in a way that reducing VOC reactivity substantially reduces the branching ratio, which results in the interesting case that for certain regimes of VOC reactivity and NO_x concentration ozone production rates increase with decreasing VOC reactivity. This is intellectually very interesting, but the paper does not present strong and convincing arguments that VOC emission reductions will actually

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reduce the branching ratio α . When looking at the data provided in the supplement, (Table S1) approximately 95% of ozone production is from substances with branching ratios α of 0.1 or less, more than 80% from substances with $\alpha \leq 0.07$. Out of the top ten ozone producers none has a branching ratio exceeding 0.1, and only two a branching ratio exceeding 0.05. In other words, most of the main ozone producers have branching ratios well below the average of 0.07. It is therefore not very likely that VOC reactivity based ozone reduction strategies will target compounds with a high a value for α , which is the condition for the hypothetical case that VOC reactivity reductions will result in increased ozone production. It cannot be ruled out that a reduction strategy targeting primarily compounds with low branching ratios may result in an over-proportional reduction in emissions of substances with large values for α , but is this a very likely scenario? In my opinion a scenario where a reduction of VOC reactivity will result in a reduction of α is equally likely to happen and there is very little evidence that supports the assumption of a connection or feedback between VOC reactivity reduction and branching ratio. It is mentioned in the paper that a scenario where reduction strategies that are unrelated to reducing VOC reactivity might result in a reduction of average α to an extent that it actually may increase ozone formation rates. This is possible, but would be primarily independent of ozone reduction strategies. It should also be considered that in the hypothetical example presented in Figure 1, the increase of ozone production rate upon reduction of VOC reactivity happens only at very high VOC reactivity and for a limited range of NO_x concentrations. Are these conditions particularly relevant are for regions with ozone control problems? In any case under these conditions VOC control would not be very efficient anyway, independent of branching ratio.

iii) VOC Emission Controls and Ozone Production

The dependence between VOC reactivity, NO_x concentration, branching ratio α and ozone production rate presented in this paper is based on atmospheric concentrations, composition of VOC mix and so on, not emissions. The connection between emissions

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and atmospheric concentration of individual VOC and NO_x is complex and depends on a number of factors, including OH-radical concentration. Changes in branching ratio α will also have consequences for atmospheric NO_x. For example an increase in branching ratio will most likely result in a reduction of atmospheric NO_x concentrations, if NO_x emissions remain unchanged. Similarly, changes in OH radical concentrations will change atmospheric VOC reactivity if the reactivity of the emissions is unchanged. These are just two examples for the complex feedback between changes in branching ratio, emissions and atmospheric concentrations of ozone precursors. Some of the statements referring to emission control and the role of the branching ratio seem too strong. Examples are: "We show that emission reductions that inadvertently reduce organic nitrate production rates will be counterproductive without concurrent reductions in NO_x or other organics."(Abstract) or "We show both in a model and with a real world example of Mexico City that the effects of AN formation can counteract the benefits of VOC controls on ozone production." (Conclusions).

Some Details In many cases the conventional form (square brackets) is used to denote concentrations. In other cases not (e.g. equations 10, 11).

In order to be consistent with (3) and (4) the correct form of (8) should be:

$$PO_3 = 2 \times (1 - \alpha) \times \tau \text{VOC} \times [\text{OH}]$$

The approximation $[\text{HO}_2] \approx [\text{RO}_2]$ in (7) is not necessary, a correct solution based on steady state and the assumption that all HO₂ and RO₂ react only with NO (which is needed anyway) can be derived. This will only require use of values already used in (10)-(12)

It is not obvious what is meant with "chain 3 propagation" (Chapter 3.1)

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