Impacts of HO$_x$ regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres

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[1] A global chemistry-climate model is used to assess the impact on atmospheric composition of the regeneration and recycling of HO$_x$ in the photo-oxidation of isoprene. The impact is explored subject to present-day, pre-industrial and future climate/emission scenarios. Our calculations show that, in all cases, the inclusion of uni-molecular isomerisations of the isoprene hydroxy-peroxy radicals leads to enhanced production of HO$_x$ radicals and ozone. The global burden of ozone increases by 25–36 Tg (8–18%), depending on the climate/emissions scenario, whilst the changes in OH lead to decreases in the methane lifetime of between 11% in the future and 35% in the pre-industrial. Critically the size of the change in methane lifetime depends on the VOC/NO$_x$ emission ratio. The results of the present-day calculations suggest a certain amount of parameter refinement is still needed to reconcile the updated chemistry with field observations (particularly for HO$_2$+RO$_2$). However, the updated chemistry could have far-reaching implications for: future-climate predictions; projections of future oxidising capacity; and our understanding of past changes in oxidising capacity. **Citation:** Archibald, A. T., et al. (2011), Impacts of HO$_x$ regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres, *Geophys. Res. Lett.*, *38*, L05804, doi:10.1029/2010GL046520.

1. Introduction

[2] Isoprene (2-methyl-1,3-butadiene) emissions comprise a major fraction of total biogenic volatile organic compound (BVOC) emissions. Field and modelling studies estimate that the natural emissions of isoprene have been fairly constant over the last decade or so, ~400–500 Tg C/yr [*Müller et al.*, 2008]. Owing to the high reactivity of isoprene towards the hydroxyl radical (OH), model studies invariably implicate isoprene as a large sink of OH. However, the reactive products formed from the oxidation of isoprene by OH, the isoprene hydroxy-peroxy radicals (ISOPOHO2), can interact with oxides of nitrogen (NO$_x$ = NO + NO$_2$) resulting in production of ozone in the troposphere—the main OH precursor.

[3] Recent field studies in major isoprene emitting regions such as Amazonia [*Lelieveld et al.*, 2008] and South East Asia [*Hewitt et al.*, 2010] have found large discrepancies between modelled and measured HO$_x$ concentrations. These discrepancies are not confined to the tropics, but coincide with regions impacted by isoprene emissions [*Hofzumahaus et al.*, 2009; *Tan et al.*, 2001]. The model-measurement disagreement is most pronounced where high isoprene concentrations (>1 ppbv) coincide with low NO$_x$ concentrations (<1 ppbv). Several theoretical [*Peeters et al.*, 2009; *Peeters and Müller*, 2010; *da Silva et al.*, 2010] and experimental [*Paulot et al.*, 2009] studies have recently provided new insights into the oxidation mechanism of isoprene. No doubt, more studies will be required to unravel its intricacies. However, the work of *Peeters et al.* [2009] concerning unimolecular reactions of ISOPOHO2, has been shown in both box model [*Archibald et al.*, 2010] and global models [*Archibald et al.*, 2010; *Stavrakou et al.*, 2010] to improve the representation of low-NO$_x$ isoprene chemistry.

[4] We use the UKCA global chemistry-climate model (http://www.ukca.ac.uk) to explore the impact of including isomerisation reactions of ISOPOHO2 on the composition of the atmosphere in the present (2000), pre-industrial (*ca.* 1850) and future (2100). There exists a great deal of work in the literature about the importance of isoprene oxidation in global chemistry [e.g., *Wang and Shallcross*, 2000], and more recently, a great deal of debate towards the issues of reconciling problems with representing its chemistry in global models [*Lelieveld et al.*, 2008; *Archibald et al.*, 2010; *Stavrakou et al.*, 2010]. There are likely to be modifications to the mechanism of isoprene oxidation as time progresses, but this work investigates the most important aspect that has been thus far poorly represented – the regeneration of HO$_x$ radicals through isomerisation reactions of ISOPOHO2.

2. Method

[5] A number of experiments with the UKCA model, run at a horizontal resolution of 3.75° in longitude × 2.5° in latitude on 60 hybrid height levels that stretch from the surface to ~84 km, were carried out. The model set up is similar to that described by *Telford et al.* [2010], with a chemical mechanism comprising 60 chemical tracers and

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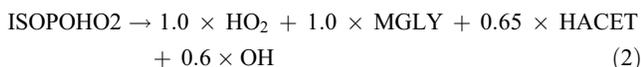[7]Department of Chemistry, University of Leicester, Leicester, UK.

Table 1. Prescribed Methane Levels (Mixing Ratios in ppmv) and Emissions for the Three Sets of Simulations[a]

	NO$_2$	CO	HCHO	C$_2$H$_6$	C$_3$H$_8$	Acetone	CH$_3$CHO	C$_5$H$_8$	CH$_4$
PI (1860)	34.3	434.7	4.1	10.2	3.7	43.8	6.7	573	0.790
PD (2000)	147	1078.1	6.3	51.1	48.5	65.3	24.2	467.1	1.655
FC (2100)	122.9	1039.5	5.7	45.8	42.3	63.1	22.4	545.3	2.973

[a]All emissions are given as global yearly averages in Tg of species emitted. See text for sources of emissions.

132 photochemical reactions, including the oxidation of isoprene based on the Mainz Isoprene Mechanism [*Pöschl et al.*, 2000]. The model's dynamical core is based on the Met Office's Unified Model version 6.1. In each experiment, the model is allowed to run freely with the climate forced by specified concentrations of long-lived greenhouse gases and ozone-depleting substances, in addition to pre-scribed sea surface temperatures and sea-ice coverage from the HadISST dataset [*Rayner et al.*, 2003]. Stratospheric chemistry is not calculated explicitly. Instead, the concentrations of ozone and NO$_y$ above 30 hPa are taken from the Cambridge 2D model [*Law and Pyle*, 1993] and are not changed between experiments, so that the influence of the stratosphere on the troposphere remains constant. The results are taken from three-year integrations following an 18 month 'spin-up' period.

[6] Our modification to the isoprene mechanism follows that applied in the global model STOCHEM, in the study of *Archibald et al.* [2010] (their reactions R24–R26). However, the representation used in this study differs somewhat from *Archibald et al.* [2010] as we omit the formation of the (predicted) highly photolabile hydroperoxy-aldehyde (HPALD) and instead assume prompt formation of OH from both isomerisations of the ISOPOHO2. The two reaction pathways are represented by equations (1) and (2) ($k_1 = 4.0 \times 10^{-3}$ s^{-1}; $k_2 = 8.0 \times 10^{-2}$ s^{-1}; MACR = lumped C4 carbonyl; MGLY = methyl glyoxal; HACET = hydroxyacetone). The product yields were determined by running a series of box model experiments and optimising the product yields to give a reasonable match to the results of Mechanism 4 of *Archibald et al.* [2010] for HO$_x$, ozone and CO. The values used for k_1 and k_2 come from *Archibald et al.* [2010], derived for conditions appropriate for the tropics. Both k_1 and k_2 are predicted to have significant temperature dependence (*Peeters and Müller* [2010] predict variations of up to a factor of 3 for a 10 K change in temperature). However, owing to the fact that most isoprene is oxidised in the tropics (near the surface) where there is small variation in temperature, it is expected that this simplification should have only a relatively small impact on the results.

$$ISOPOHO2 \rightarrow OH + MACR + HCHO \qquad (1)$$

$$ISOPOHO2 \rightarrow 1.0 \times HO_2 + 1.0 \times MGLY + 0.65 \times HACET + 0.6 \times OH \qquad (2)$$

Six experiments were carried out: a Base run (B) and a Modified run (M; including the isomerisation reactions of ISOPOHO2) each subject to Present-Day (PD), Pre-Industrial (PI) and Future (FC) climate/emissions scenarios (see Table 1 for a breakdown of the emissions), based on the emissions of *Stevenson et al.* [2006], *Lamarque et al.* [2010] and *Dentener et al.* [2005] respectively. The future emissions reflect the IPCC B2+CLE scenario. Note the relatively similar total BVOC emissions, but much lower total NO$_x$ emissions, in the pre-industrial, compared with the present-day. In all cases the amount of CH$_4$ is prescribed (Table 1). In each period, we assessed the impact of the updated isoprene scheme in terms of absolute differences (i.e., M − B) and percentage differences (i.e., 100 × ((M − B)/B)). We assessed the changes in the troposphere only and define this layer based on the lapse rate.

3. Results

3.1. Present Day

[7] In general our base present-day simulation (PD-B) generates results for ozone and CO that are consistent with a wide range of observations and compare well with other global models (Figure 1) [cf. *Stevenson et al.*, 2006; *Shindell et al.*, 2006]. A comparison against ozone-sonde measurements is shown in Figure 1a (PD-B indicated by red line and pink envelope). In general, and in line with the majority of models [e.g., *Shindell et al.*, 2006], the PD-B simulation tends to under-predict CO in the Northern Hemisphere and slightly over predict CO in the Southern Hemisphere (red line in Figure 1b). Including the ISOPOHO2 isomerisation reactions (PD-M, indicated by blue line and purple envelope in Figure 1a) leads to an improvement in the comparison with ozone for almost all latitude and pressure bands (the exception being Equator-30°N, 750 hPa). Likewise, there is improved simulation of CO and the SH high bias is slightly reduced in the PD-M simulation (blue line in Figure 1b). The levels of OH and HO$_2$ are enhanced by as much as 410% and 225% respectively in certain regions at the surface and up to 75% (for OH) in the zonal mean (Figure 2). These enhancements are approaching those needed to reproduce the high concentrations of OH and HO$_2$ measured in the tropics [*Lelieveld et al.*, 2008]. Note that the greatest increases in OH are mainly limited to surface regions in the tropics, where there are high emissions of isoprene but low emissions of NO$_x$. Figure 2d clearly shows that surface increases are propagated throughout the tropical free troposphere. These increases in the free troposphere are driven by convection in the tropics lifting the products of isoprene oxidation (such as MGLY in equation (2)) to higher altitudes where rapid photolysis allows enhanced production of HO$_2$. In our parameterisation of the products of the ISOPOHO2 isomerisation's MGLY is included as a major product. Our PD-M simulation tends to predict concentrations of MGLY which are comparable but higher (around a factor of two) than those reported by *Fu et al.* [2008]. The exact products following ISOPOHO2 isomerisation's are in need of experimental verification. However, our representation of them as small oxidised compounds known to be associated with isoprene oxidation should, to first order, have only a small effect on the results.

[8] In Figure 1c we compare modelled and measured OH and HO$_2$+RO$_2$ made during the OP3 campaign in Borneo
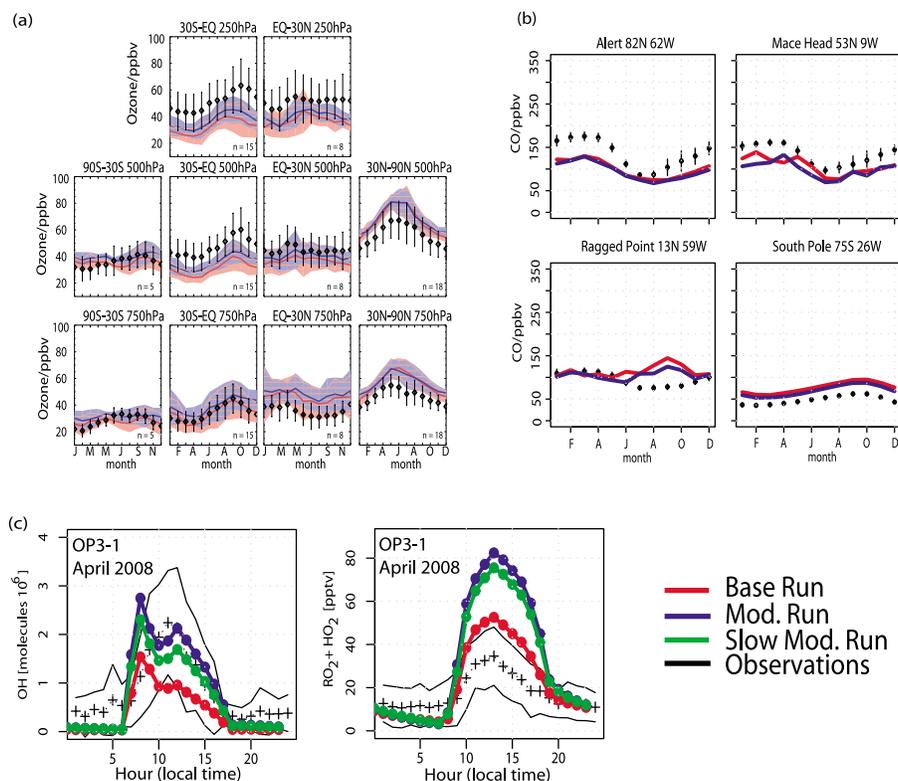
Figure 1. Comparison of PD results with observations. (a) Comparison with ozone-sonde data (data from *Logan* [1999] and *Thompson et al.* [2003a, 2003b]). (b) Comparison with surface CO measurements (data from the NOAA GMD network [*Novelli et al.*, 1998]). (c) Comparison with surface observations made during the OP3 campaign in Borneo. OH data are measured using Leeds FAGE instrument [*Whalley et al.*, 2010], RO$_2$+HO$_2$ are measured using Leicester PERCA instrument [*Fleming et al.*, 2006]. In all cases observations are given by black lines and symbols, with the PD-B data given by red lines and dots and the PD-M data by blue lines and dots. Sensitivity simulations are shown in Figure 1c for reducing the rates of $k_1 + k_2$ by half (green lines).

[*Hewitt et al.*, 2010]. The PD-M simulation (blue line) clearly improves the comparison between modelled and measured OH. Reducing the rate of the ISOPOHO2 isomerisation's by a factor of two (green lines) leads to a very small decrease in the OH enhancement compared with the PD-M run. However, it is apparent from analysis of the HO$_2$+RO$_2$ data that some form of parameter refinement is needed as the PD-M mechanism over simulates the amount of HO$_2$+RO$_2$ by more than a factor of two. We note that this is not unique to our implementation of the Peeters' mechanism; both *Stavrakou et al.* [2010] and *Whalley et al.* [2011] also present results that show an over-simulation of HO$_2$ relative to OH. Globally, the amount of OH in the troposphere increases significantly (Table 2) leading to a decrease in the lifetime of methane, of around 14%. The amount of ozone also increases by some 25 Tg (8%) globally. This is driven by a reduction in the flux of ozonolysis and by an increase in the flux through the reaction between HO$_2$ and NO. The level of enhancement in HO$_x$ in the present study is much greater than that reported by *Archibald et al.* [2010] where at most they calculated increases of ~50%. This can be attributed to an overestimation in that study of NO$_x$ in isoprene rich areas, with the present results being more in line with the work of *Peeters and Müller* [2010] and *Stavrakou et al.* [2010].

3.2. Pre-industrial

[9] As in previous studies [*Mickley et al.*, 2001; *Lamarque et al.*, 2005], our base pre-industrial calculations (PI-B) cannot reproduce the very low concentrations of surface ozone measured at the turn of the 20th century using the Schonbein method [*Pavelin et al.*, 1999]. *Mickley et al.* [2001] suggested this could be the result of an overestimation of NO$_x$ emissions at that time. They also postulated that increased emissions of reactive BVOCs could contribute, although *Lamarque et al.* [2005] have subsequently argued that this would be inconsistent with our best estimates of PI emissions. More recently, *Parrella et al.* [2010] have reported that the inclusion of tropospheric halogen chemistry can help to resolve this.

[10] Like *Mickley et al.* [2001], we find that the combination of low levels of NO$_x$ and the propensity for isoprene to react with OH leads to near titration of OH in much of the continental boundary layer in the tropics and mid-latitudes in our PI-B experiment. When we include the updates to the chemistry (PI-M), as with the present-day, we calculate significant enhancements in OH and HO$_2$, but in the pre-industrial this is to a much greater extent owing to the lower levels of NO$_x$. We calculate enhancements in OH approaching 1500% in some regions at the surface, and 170% in the zonal mean (in the tropics near the surface, see Figure 2); HO$_2$ is enhanced by as much as 300% at the surface and
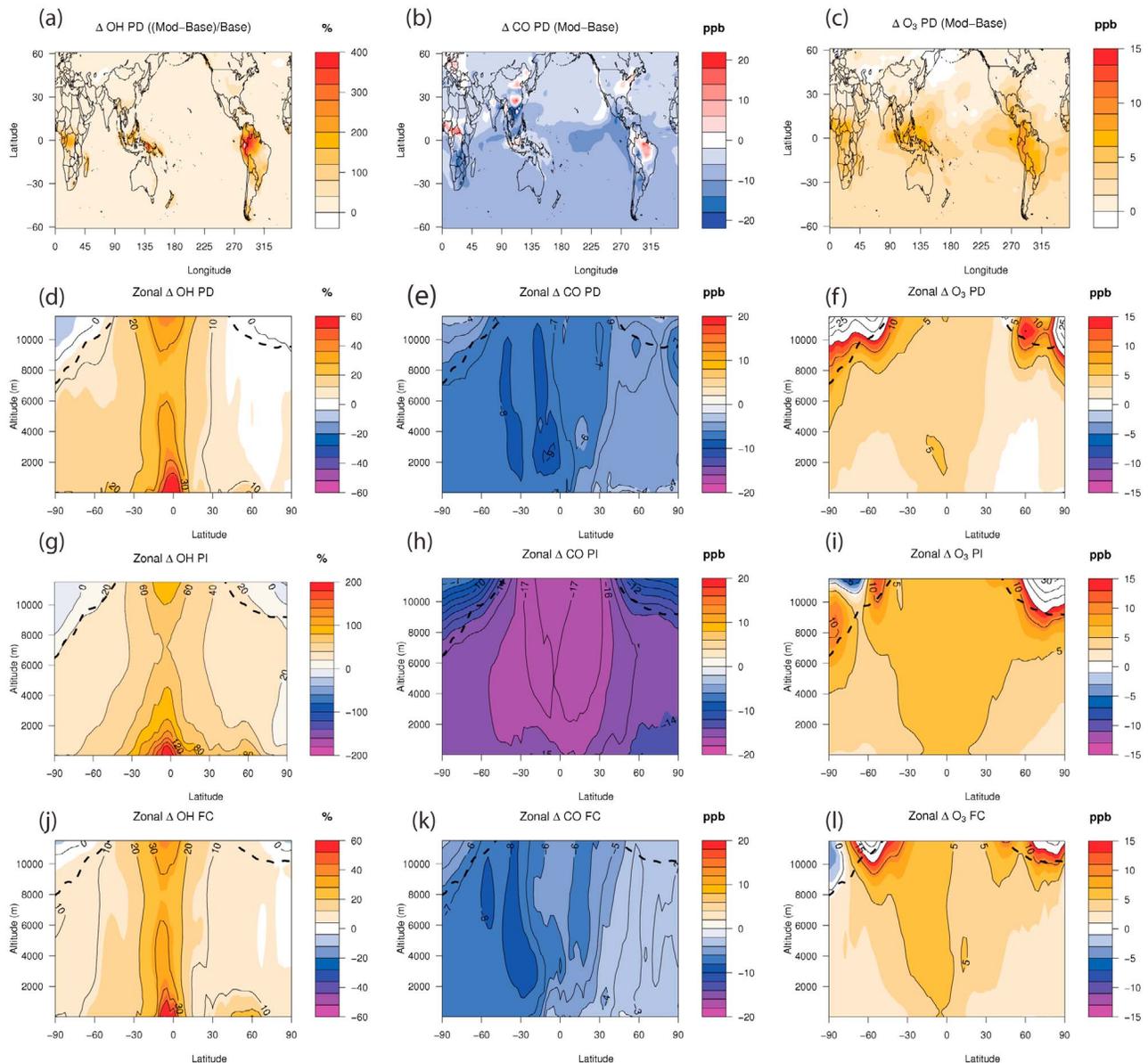
Figure 2. Multiannual mean surface (less than 600 m) and zonal changes in OH, CO and O$_3$ between Modified run and Base run for three climate/emission scenarios. Changes in O$_3$ and CO are expressed as absolute changes (Mod-Base), changes in OH presented as percentage changes ((Mod − Base)/Base) × 100. Surface changes shown for PD conditions only. Zonal plots have the respective height of the tropopause superimposed (thick black dashed line) for each scenario. (Note figures are clipped in height to focus attention on the effects in the troposphere.)

75% in the zonal mean. Enhanced destruction of CO in the boundary layer leads to lower levels of CO, and higher levels of OH, throughout much of the troposphere. Globally, the increase in OH leads to a 35% reduction in the lifetime of methane—a very substantial decrease—whilst we calculate an increase in global ozone burden of 36 Tg (18%).

3.3. Future

[11] We explored a reasonably optimistic future-emissions scenario (IPCC B2+CLE), in which NO$_x$ emissions decrease but VOC emissions increase. We note that the increased emissions of isoprene do not reflect the important role that CO$_2$ inhibition may play in a CO$_2$-warmed future [*Young*

Table 2. Tropospheric Burdens of O$_3$, OH and CO for Each Model Run[a]

Run	Ozone Burden (Tg)	OH Burden (Tg)	CO Burden (Tg)
PI–B	194	7.74×10^{-5}	347
PI–M	230	1.16×10^{-4}	280
PD–B	323	1.15×10^{-4}	432
PD–M	348	1.34×10^{-4}	404
FC–B	347	1.04×10^{-4}	567
FC–M	380	1.21×10^{-4}	543

[a]Troposphere defined using lapse rate tropopause (see Figure 2).

et al., 2009]. The results of the base simulation (FC-B) are generally similar to the PD-B simulation, although we simulate an increase in ozone of ~32 Tg. Similarly, on updating the chemistry (FC-M) we calculate enhancements in OH and HO_2 of as much as 550% and 200% respectively at the surface and greater than 75% for OH in the tropics near the surface as a zonal mean (see Figure 2). The increased HO_x then leads to further increases in ozone burden (32 Tg or ~9%) and a significant reduction in the lifetime of methane of ~11%.

4. Discussion and Conclusions

[12] Implementing updated (low NO_x) chemistry for isoprene has led to large increases in modelled HO_x concentrations. These increases are largest within the boundary layer in regions where NO_x concentrations are low and isoprene concentrations are high. These areas are predominantly found in the tropics. Deep convection in these areas lifts the products of isoprene oxidation into the free troposphere and promotes ozone production (mainly through an increase in the reaction between HO_2 and NO). Ultimately, the modified isoprene chemistry is sensitive to the chemical environment which can be characterised on a global scale by the ratio of VOC/NO_x emissions. Characterising the global effects of this modified chemistry by comparing relative changes in the methane lifetime shows that there is a tailing off in the importance of the effect, from the pre-industrial to a warmer, "cleaner" future. However, the importance of understanding the evolution in atmospheric composition should not be underestimated. The changes in ozone burden (Table 2) (and to a lesser extent methane lifetime) have bearings on future-climate predictions, owing to the radiative-forcing properties of these greenhouse gases, whilst the changes in methane lifetime have consequences for projections of future oxidising capacity, and our understanding of past changes in oxidising capacity—an area we intend to explore further. The Peeters mechanism [*Peeters et al.*, 2009] is unlikely to be the last word on the subject but its contribution to our understanding of the chemistry surrounding isoprene oxidation at low-NO_x concentrations has potentially far-reaching implications. These warrant further study and validation via model-measurement comparison and crucially targeted laboratory experiments aimed at simulating the conditions encountered in the tropical boundary layer.

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