

HO_x radical regeneration in isoprene oxidation *via* peroxy radical isomerisations. II: experimental evidence and global impact†

Jozef Peeters*^a and Jean-François Müller^b

Received 22nd March 2010, Accepted 24th August 2010

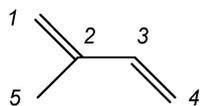
DOI: 10.1039/c0cp00811g

A consistent body of experimental evidence from work of other groups is presented in support of the novel, theoretically based, isoprene oxidation mechanism we recently proposed to rationalize the unexpectedly high OH concentrations observed over areas with high isoprene emissions. Some explicit or implicit criticisms on the new mechanism are addressed. A particular photochemical mechanism is newly proposed for the OH-regenerating photolysis of the crucial hydroperoxy-methyl-butenals (HPALDs), formed by isomerisation of the initial isoprene hydroxy-peroxy radicals, that rationalizes a quantum yield close to 1. A similar photolysis mechanism of the resulting photolabile peroxy-acid-aldehydes (PACALDs) is shown to generate ample additional OH. Global modeling demonstrates the major importance of the new chemistry for the oxidizing capacity of the atmosphere over continents. The globally averaged yield of the HPALDs in the oxidation of isoprene by OH is estimated to be of the order of 0.6. The isomerisation reactions of isoprene peroxy radicals are found to result in modelled [OH] increases in the planetary boundary layer by up to a factor of 3, in agreement with the reported observations as in the Amazon basin.

Introduction

Recently,¹ we proposed and theoretically quantified novel, HO_x-regenerating pathways for the OH-initiated oxidation of isoprene to explain the much higher than modeled OH radical concentrations measured in many campaigns in forested areas with high isoprene emissions, such as the St Lawrence basin (PROPHET),² Northern Greece (Pertouli),³ the Amazon basin (GABRIEL),^{4,5} the Pearl River Delta, China (PRIDE),⁶ the Eastern US (INTEX-A),⁷ and Malaysian Borneo (OP3-1).⁸ Major HO_x radical (re-)generation in the oxidation of isoprene, with its huge emissions of 500 Tg per year,⁹ is expected to have a large impact on the oxidizing capacity of the atmosphere.⁴

The new reaction pathways we put forward and characterized using high-level quantum chemical and statistical rate theories¹ are presented schematically in Fig. S1 and S2 of the ESI.† These schemes consider the two major OH-adducts to the terminal carbons of CH₂=C(CH₃)-CH=CH₂, which—owing to their allyl-resonance—result in four isoprene hydroxyperoxy radical isomers (ISOP-OH-OO).^{10,11} All relevant radicals are denoted further by the carbons 1 to 4 (see Scheme below) to which the OH and OO groups are bound.



^a Department of Chemistry, K.U.Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium. E-mail: Jozef.Peeters@chem.kuleuven.be; Fax: +32 16-327992

^b Belgian Institute for Space Aeronomy, Avenue Circulaire 3, B-1180, Brussels, Belgium

† Electronic supplementary information (ESI) available: Details on the newly proposed mechanisms—constituting a first outline of the *Leuven Isoprene Mechanism (LIM)*—and on the experimental evidence in their support. See DOI: 10.1039/c0cp00811g

For example, 1-OH-2-OO• denotes the β-OH-peroxy radical HOCH₂-C(CH₃)(OO•)-CH=CH₂ while Z-1-OH-4-OO• denotes the *Zusammen* conformer of the δ-OH-peroxy radical HOCH₂-C(CH₃)=CH-CH₂OO•, formed both from the allyl-stabilized 1-OH adduct HOCH₂-C•(CH₃)-CH=CH ↔ HOCH₂-C(CH₃)=CH-CH•.

The four newly proposed crucial pathways in isoprene oxidation¹ are first summarized.

(i) The allyl-stabilised major OH-isoprene adducts to the two terminal carbons, 1-OH and 4-OH, bind O₂ only weakly (18–23 kcal mol⁻¹); as a consequence, the resulting isoprene hydroxyperoxys eliminate O₂ so fast—at predicted 303 K rates of order 1 to 10 s⁻¹—that the various isomers/conformers can readily interconvert *via* O₂-re-addition, to a near-equilibrium population, such that the bulk of the reactive flux of a given peroxy pool can be channeled through its most reactive isomer/conformer.¹ Note that this cannot occur when the peroxys react very fast, *i.e.* at NO-levels ≥ 500 ppbv as in most laboratory studies.

(ii) The β-OH-peroxys 1-OH-2-OO• and 4-OH-3-OO•, which are the most stable peroxy-isomers from the initial 1-OH and 4-OH adducts, can undergo concerted 1,5-H-shifts to directly re-generate OH with HCHO and methyl-vinylketone (MVK) or methacrolein (MACR) as co-products, at predicted rates of order 0.01 s⁻¹ at 303 K.¹ Note that the lower rates, reported in another recent study,¹² result mainly from its over simplified treatment of tunneling that is evaluated for the endothermal “first step”, instead of for the quasi-thermoneutral overall process.¹

(iii) For both the major initial 1-OH and 4-OH radicals, the resulting Z-δ-OH-peroxy isomers/conformers, Z-1-OH-4-OO• and Z-4-OH-1-OO• respectively, were predicted to be exceptionally reactive and to dominate the overall mechanism by their fast 1,6-H shifts, with 303 K rates of order 1 to 10 s⁻¹, which *via* subsequent reaction with O₂ generate HO₂ plus the

Z-hydroperoxy-methyl-butenals $\text{OCH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{OOH}$ or $\text{OCH}-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2\text{OOH}$ (denoted below as HPALDs).¹

These particular 1,6-H shifts are assisted by allyl-stabilization of the product radicals (see ESI†), explaining their much higher rates compared to the experimental $k(1,6\text{-H})$ (298 K) of 0.03 s^{-1} for $\text{HOCH}_2-[\text{CH}_2]_2-\text{CH}(\text{OO}^\bullet)-\text{CH}_3$ measured by Perrin *et al.*¹³ We estimated that in the conditions of the GABRIEL campaign^{4,5} process (iii) generates $0.68^{+0.15}_{-0.25}$ $\text{HO}_2 + \text{HPALDs}$ per $\text{OH} + \text{isoprene}$ addition step. This high yield is only possible by the very fast interconversion of the peroxy isomer/conformers above, as the steady-state $Z-\delta\text{-OH-peroxy}$ populations make up only 5% of the total.

(iv) Equally crucial, we hypothesised that the HPALDs, owing to their particular combination of a near-UV absorptive conjugated $\text{O}=\text{C}-\text{C}=\text{C}$ chromophore and a very weak $\text{O}-\text{OH}$ bond, can photodissociate quickly into OH and a reactive radical that may give rise to additional (photo)-production of OH .¹

At this point, it should be stressed again that the probable error on the theoretically quantified rates¹ of the newly proposed peroxy reactions (i)–(iii) is a factor of ~ 5 , due mainly to the possible error of 1 kcal mol^{-1} on even the high-level CBS-APNO computed dissociation energies and barrier heights.¹ In this context, the substantial and unexpected differences between the two $k(1,6\text{-H})$ rate coefficients as well as between the two $k(1,5\text{-H})$ appear largely artificial, likely due in part to imperfect B3LYP relative energies of the dominant reactant- and transition state conformers. In the present work, an identical rate coefficient $k(1,6\text{-H})$ will be adopted for both $Z-\delta\text{-OH-peroxys}$, equal to the geometric average of the two first-principles values¹ (see the $k(T)$ expressions in Table S1 of the ESI†); note however that this leaves the HPALD + HO_2 yield nearly unchanged. Similarly, identical $k(1,5\text{-H})$ values for the two $\beta\text{-OH-peroxys}$ are used further in this work, but with an additional and substantial modification required by experimental evidence (see below). The various product yields displayed in Fig. 1 are calculated with the adapted rate coefficients, listed in Table S1 of the ESI.†

Yet, it need likewise be emphasised that the overall $\text{HO}_2 + \text{HPALDs}$ yield *via* mechanism (iii) is only mildly sensitive to the rates of the reactions involved. For example, varying the key kinetic parameters by factors 3 and 0.33 was found to result in departures of only $+0.15$ and -0.25 from the first-principles yield of 0.68 in GABRIEL conditions.¹ The non-linear dependence of the yields on the reaction rates is also illustrated in Fig. S3–S6 of the ESI†, and is also discussed further below.

It should also be noted that the rate coefficients for O_2 -elimination, $k_{-\text{O}_2}(T)$; for the 1,5-H shifts, $k(1,5\text{-H})(T)$; and for the 1,6-H shifts, $k(1,6\text{-H})(T)$, are all strongly temperature-dependent, changing by factors 2–3.5 for a T change of 10 K. The theoretically derived values given in the previous communication¹ were for $T = 303 \text{ K}$, while $k(T)$ expressions were listed in the ESI of that paper.

In this work, we will first discuss and rationalize the highly non-linear behavior of the $\text{HO}_2 + \text{HPALDs}$ yield with respect to the $k(1,6\text{-H})$ rate coefficients of the $Z-\delta\text{-OH-peroxys}$, as it is of major importance for the new isoprene mechanism in

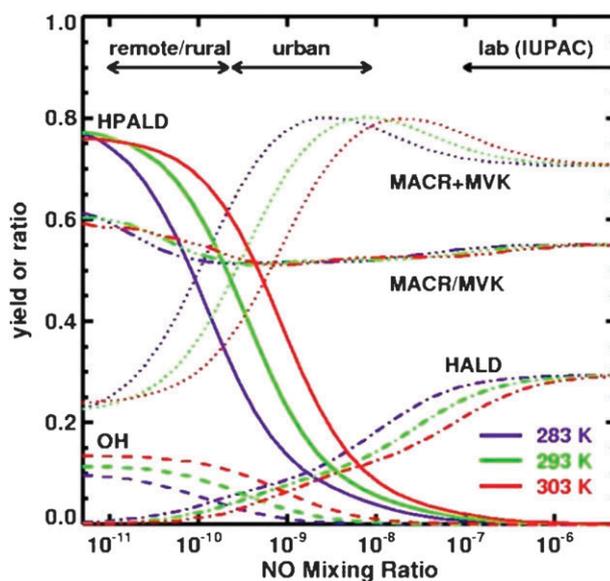


Fig. 1 Primary yield of HPALD (solid lines), OH (dashed), the sum $\text{MVK} + \text{MACR}$ (dotted) and the hydroxy-aldehydes HALD (dash-dotted), in the oxidation of isoprene by OH , as a function of NO , at three temperatures. For simplicity, the reactions of the isoprene-peroxys with HO_2 and RO_2 were neglected in the calculations. The MACR/MVK yield ratios are also shown. Typical NO concentration ranges in remote/rural, urban and laboratory conditions are also indicated.

atmospheric conditions. Secondly, we will address a number of recently reported findings that appeared to be at odds with our newly proposed chemistry or question its importance, as well as results that called for reasonable adaptations of some of the first-principles-based rates. Altogether, from the body of observations and data available in the literature, we will present consistent evidence for all new pathways in our proposed mechanism, including fast HPALD photodissociation. For the latter, we will propose a new, highly efficient mechanism that produces OH and a co-product radical of which the specific subsequent chemistry generates ample additional OH . Finally, in a modeling study, the first-generation product distribution for the revised isoprene chemistry will be examined as a function of the NO level. A parameterized form of the new oxidation pathways will be implemented into a global tropospheric chemistry-transport model, in order to determine their importance for the distributions of HO_x in the troposphere. The calculated impacts over the Amazon basin will be evaluated against the GABRIEL campaign measurements,⁴ and compared with a previous modeling study.¹⁴

Experimental evidence

Non-linear dependence of the hydroperoxy-methyl-butenal (HPALDs) + HO_2 yields on the $Z-\delta\text{-OH-peroxy}$ 1,6-H shift rates

Of high relevance for the following discussion is the striking non-linearity of the HPALDs + HO_2 yield with respect to the $k(1,6\text{-H})$ shift rates of the $Z-\delta\text{-OH-peroxys}$, as depicted in

Fig. S3 of the ESI.† This remarkable behavior is due to the quasi-equilibrium between the three isomers/conformers for each of the two peroxy pools, as a result of the fast O_2 -elimination from the peroxy radicals outrunning the product-forming steps for both the most stable and the least reactive isomers, *i.e.* the β -OH- and E - δ -OH-peroxys. The combined population of these two isomers/conformers approaches 95% for each pool, quasi-independent of the HO_2 and NO concentrations (up to ~ 500 ppt; see ESI†) and nearly insensitive to the $k(1,6-H)$. Since a variation of the $k(1,6-H)$ can act only through the minor Z - δ -OH-peroxys ($\sim 5\%$ of the total population), it can only slightly affect the total peroxy concentration and therefore only moderately affect the reactive flux through the β -OH- and E - δ -OH-peroxys, and hence also the flux through the Z - δ -OH-peroxy 1,6-H shifts, as the total reactive flux is a constant at given isoprene and OH concentrations.

Initial branching between the E - and Z - δ -OH-peroxy conformers

It was recently commented¹⁵ that the initial branching ratio of 1 : 1 : 8 between the E - and Z -1-OH-4-OO• and 1-OH-2-OO• isomers suggested in the recent study of Ghosh *et al.*¹⁶ is at odds with the ratio of 0.63 : 3 : 6.3 that we adopted.¹ First, as we extensively discussed,¹ our branching ratios are actually based primarily on the experimental isoprene oxidation products distributions at high NO levels, on which there is a wide consensus.^{11,17} Second, the present results of Ghosh *et al.* are in sharp conflict with conclusions of earlier studies by that group—based on a well conceived and well argued OD/OH-isotopes cycling experiment—that the branching to the Z - δ -OH-peroxy is nearly 10 times that to the E -counterparts.¹¹ The crux of the theoretically backed^{18,19} argumentation¹¹ is that at high NO the Z - δ -OD-peroxys finally yield deuterated OD and C_5 -hydroxycarbonyls (*i.e.* hydroxy-aldehydes or HALDs) whereas the E - δ -OD-peroxys form OH and C_4 -hydroxycarbonyls, along with HCHO. Therefore also, the 20–30% C_5 -hydroxycarbonyl yields at high NO reported by many groups^{11,17} *versus* only a few % of the C_4 -counterparts (see ref. 11), strongly contradicts the Ghosh *et al.* conclusions, while consistent with our adopted branching. Third, different from the statement in the Ghosh *et al.* paper, Dibble's earlier computational work¹⁹ did not predict a nearly equivalent branching for the E - and the Z -isomers of the δ -hydroxy-peroxy radical channels, but instead estimated a 50 : 50 branching between the initial E - and Z -isomers of the *initial* 1-OH-isoprenyl *adduct*—for which we obtained the same result, but using the notations *trans*- and *cis* 1-OH-isoprene (see ESI† and ref. 1). It is important to remind that isoprene itself is present as the *trans* conformer only and that it is the high initial internal energy content of 40 kcal mol⁻¹ released by the OH-addition that enables the activated *trans* hydroxy-adduct to initially promptly convert into the *cis* form over the ~ 15 kcal mol⁻¹ high barrier to rotation.^{1,19} As the densities of states of the *trans*- and *cis* 1-OH-isoprene adducts are nearly equal at the high initial energies, collisional stabilisation results in a nearly 50 : 50 ratio when reacting with O_2 after ~ 0.1 μ s. It must be noted that in the Ghosh *et al.* work,¹⁶

the 1-OH-isoprenyl radicals were not generated by OH addition to isoprene but by photolysis of 2-iodo-2-methyl-but-3-en-1-ol; the apparently divergent *E*- *versus* Z -1-OH-4-peroxy branching in this experiment could therefore be due to a (much) lower internal energy content of the nascent 1-OH-isoprenyl radical which could result in preferential stabilisation as the *trans* (or E) 1-OH-isoprenyl “adduct”.

Remarkably—the more so as unnoticed so far—the C_5 -hydroxy-aldehydes (HALDs) found to be produced in many studies at NO levels ≥ 100 ppbv with overall yields of $\sim 25\%$, from the Z - δ -hydroxyperoxys,^{11,17} have, to our knowledge, never been reported as significant oxidation products at NO levels ≤ 1 ppbv, neither in field campaigns nor in photoreactor studies. As an example, in the “SAPHIR” photoreactor work of Karl *et al.*²⁰ at 200–600 pptv NO, MVK and MACR were determined, with yields of 41% and 27%, respectively, but HALDs were not reported, though their MIM²¹-based mechanism²² predicts HALD yields even over 40%. Neither were HALDs reported in the Amazon basin campaign of Karl *et al.*²³ at NO levels estimated at 100–300 pptv, whereas MVK, MACR—and even hydroxyacetone with yield $< 10\%$ —were detected and quantified.

Importantly, our newly proposed chemistry¹ *predicts* very low HALD yields for NO ≤ 1 ppbv. In such conditions the fast interconversion of the peroxy isomers/conformers leads to a near-equilibrium population with only some 5% Z - δ -hydroxyperoxys, which in addition isomerise *via* the 1,6-H shifts far faster than they react with NO (and/or RO_2). Thus, as shown in Fig. 1, *e.g.* at 400 pptv NO our model predicts an HALD yield $\leq 5\%$, *versus* $\sim 50\%$ MVK + MACR. The absence of any reports on HALDs as isoprene oxidation products at low NO is therefore consistent with our proposed chemistry.

1,5-H and 1,6-H shift reactions of ISOP-OH-OO peroxy radicals

Recently, Paulot *et al.*²⁴ reported findings highly relevant to the issues at hand, in photoreactor isoprene oxidation experiments ($T = 290$ – 295 K), with OH and HO_2 radicals generated by “blacklight” UV-photolysis of *ca.* 1.75 ppmv H_2O_2 , with $J = 2.15 \times 10^{-6} s^{-1}$, followed by $OH + H_2O_2 \rightarrow HO_2 + H_2O$. The initial [Isoprene], in ultra-zero air, was 35 to 94 ppbv, while [OH] was of order $1 \times 10^6 cm^{-3}$ and [HO_2] as high as $5 \times 10^9 cm^{-3}$ (see their Supporting Online Material (SOM)²⁴). According to the authors, their system was quasi-NO-free at longer reaction times.

This work mainly showed that the ISOP-OH-OOH hydroperoxides, formed in reactions of HO_2 with the ISOP-OH-OO hydroxyperoxys, react fast with OH to yield epoxides while regenerating OH, a plausible pathway to precursors of secondary organic aerosol from isoprene and a route that can also bridge a (small) part of the gap between measured and modeled OH concentrations at high [Isoprene] and low [NO].

Paulot *et al.* also observed MVK + MACR production from isoprene with overall yield near 12% in NO-free conditions, and attributed it to the 1,5-H shifts proposed by us for the two major β -OH-peroxys,¹ so providing the first evidence for our route (ii). However, MVK + MACR yields

of $\sim 10\%$ in their conditions require that both $k(1,5\text{-H})$ rate coefficients are ~ 5 times higher than the geometric average of our first-principles predictions.¹ This is not unexpected, as the computed barriers for these complex concerted processes were found to be lower when using higher levels of theory (ESI†). Note that the factor of 5 is obtained when adopting a rate constant of $1.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for the competing $\text{HO}_2 + \text{ISOP-OH-OO}$ reactions as measured by Boyd *et al.*,²⁵ also taking $T = 293 \text{ K}$ ²⁴ and allowing for 2–3% MVK + MACR formation from reactions of ISOP-OH-OO with (acetyl-)peroxy radicals.

Furthermore, and of key importance for the issues at hand here, Paulot *et al.* reported observation of the HPALDs we predicted as first-generation product, but with a “yield” less than 10% of the hydroperoxides. Given their conditions, this would imply that the average $k(1,6\text{-H})$ rate coefficient of the $Z\text{-}\delta\text{-OH-peroxys}$ at $\sim 293 \text{ K}$ is only about 0.05 s^{-1} , or 30 times lower than our predictions, which would relegate our entire mechanism¹ to only a minor role in all atmospheric conditions.

Our interpretation for the low HPALD/ISOP-OH-OOH ratio in the Paulot *et al.* experiments is—besides the unusually fast ISOP-OH-OOH production due to their very high $[\text{HO}_2]$ —the order of magnitude faster removal of the HPALDs compared to ISOP-OH-OOH. Indeed, using the experimental (initial) $[\text{OH}]$ of $ca. 8 \times 10^5 \text{ cm}^{-3}$ (see below) and $k_{\text{OH}+\text{ISOP-OH-OOH}} = 7.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ derived by the authors, the removal rate of the hydroperoxides is $6.4 \times 10^{-5} \text{ s}^{-1}$, whereas, anticipating on the next section, we can expect an HPALD photolysis rate in their conditions of $J \approx 3.5 \times 10^{-4} \text{ s}^{-1}$ and, adding removal by OH, a total removal rate of $\sim 4 \times 10^{-4} \text{ s}^{-1}$ —entailing also a fast approach to the steady-state [HPALD]. Note that to evaluate $J(\text{HPALD})$, the absolute spectral flux $F(\lambda)$ of the specified photoreactor UV-blacklights was duly scaled on the basis of their stated $J(\text{H}_2\text{O}_2 \rightarrow 2 \text{ OH})$ of $2.15 \times 10^{-6} \text{ s}^{-1}$ (SOM²⁴).

Moreover, and consistent with the above, our re-analysis of the Fig. 1 data of Paulot *et al.* leaves the fate of $ca. 25\%$ of the formed ISOP-OH-OO peroxy radicals unexplained, this for reaction times $t \geq 3 \text{ h}$ when over 50 ppbv isoprene is removed and almost all of the initial $\sim 1 \text{ ppbv}$ NO_x should be sequestered as nitrates. We took the total ISOP-OH-OO formation rate (see ESI†) equal to $-\text{d}[\text{ISOP}]/\text{d}t$ derived from the [Isoprene] vs. t profile, but reduced by a factor 0.96 to allow for $\sim 4\%$ OH addition to a central carbon resulting directly in 4-penten-2-one.²⁶ The $[\text{OH}]$ was found from $-\text{d}[\text{ISOP}]/\text{d}t = k_{\text{pr}} \times [\text{ISOP}] \times [\text{OH}]$ with $k_{\text{pr}} = 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.¹⁷ The rate of ISOP-OH-OO removal by HO_2 was obtained as $\text{d}[\text{ISOP-OH-OOH}]/\text{d}t + 7.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \times [\text{OH}][\text{ISOP-OH-OOH}]$, *i.e.* with $k_{\text{ISOP-OH-OOH}+\text{OH}}$ slightly reduced to account for $\sim 7\%$ ISOP-OH-OO regeneration in this reaction (SOM²⁴). All other ISOP-OH-OO sinks considered by Paulot *et al.*, including any peroxy reactions with some remaining NO, should result in: either MVK or MACR with reported summed yield of 12%; or a diol with measured yield of 2%; or a hydroxycarbonyl (HALD or isomer) with yield implied to be minor compared to that of MVK and MACR (SOM²⁴) and assumed here as 3%; adding up to a total yield of 17%. In this way (see ESI†, Table S2),

from their Fig. 1 data, we find that $25 \pm 1\%$ of the formed peroxy radicals are unaccounted for at times $t = 3, 4$ and 5 h .

Since the HPALDs have been detected—despite their short photolysis lifetime—it is very likely that the missing peroxy radical removal path is our proposed 1,6-H shift of the $Z\text{-}\delta\text{-hydroxyperoxys}$ resulting in $\text{HO}_2 + \text{HPALDs}$.¹ To estimate the contribution of this pathway in the conditions of Paulot *et al.* using our (modified) $k(1,6\text{-H})(T)$ data (see ESI†, Table S1), a temperature of 293 K was adopted (SOM²⁴) while $[\text{HO}_2]$ was estimated at $ca. 3.3 \times 10^9 \text{ cm}^{-3}$ (at $t = 4 \text{ h}$) based on the stated $[\text{H}_2\text{O}_2]$ and $J(\text{H}_2\text{O}_2)$, the known $[\text{OH}]$ (see above), and the relevant kinetics data¹⁷ for the dominant HO_x reactions; this $[\text{HO}_2]$ estimation approach including the adopted $J(\text{H}_2\text{O}_2)$ value was verified for the one mixture for which their $[\text{HO}_2]$ was given (SOM²⁴). In this way, the contribution of the 1,6-H shifts is predicted to be $37 \pm 15\%$, compatible with the estimated “missing” fraction above.

Karl *et al.*²³ (see above) reported a measured MVK/MACR ratio of 1.34 ± 0.1 and stated that our reaction mechanism¹ predicts a too high ratio of ~ 8 (in some conditions), suggesting also that to fit their data, the contributions of the peroxy isomerisation routes should be reduced by a factor of 3. First, it should be noted that the absolute MVK and MACR yields from our mechanism are quite sensitive to T and even more so to the NO level, in particular in their estimated 100–300 pptv NO range (see Fig. 1). Nonetheless, the reason why our original rate data could underpredict MACR formation was the very high $k(1,6\text{-H})(303 \text{ K})$ of 8 s^{-1} for $Z\text{-}4\text{-OH-1-OO}^\bullet$ (vs. only 1 s^{-1} for $Z\text{-}1\text{-OH-4-OO}^\bullet$),¹ thus channeling most of the reaction flux from the 4-OH-isoprene radicals to HPALD + HO_2 . Taking both $k(1,6\text{-H})$ equal to the geometric average of their original values and both $k(1,5\text{-H})$ to 5 times their original average has resolved most of this discrepancy, with predicted MVK/MACR yield ratios now ~ 2 (see Fig. 1).

With respect to MVK and MACR production, the photoreactor study of Karl *et al.*²⁰ deserves more attention, as they derived the absolute yields of these two compounds, as $41 \pm 3\%$ and $27 \pm 3\%$, respectively, in well characterized conditions where physical removal processes and separation effects are negligible or at best minor. Our predictions for their conditions, 294 K and 400 pptv NO on average, with the “standard” $k(1,5\text{-H})(T)$ and $k(1,6\text{-H})(T)$ expressions adopted in this work, are MVK, MACR and HPALDs yields of 0.36, 0.19 and 0.40, respectively. The measured MVK and MACR yields are better reproduced by halving the $k(1,6\text{-H})(T)$, which then results in 0.44 MVK, 0.22 MACR and 0.28 HPALDs yields. However, a better agreement with the measured yields might also be achieved in other ways, since the product yields for this complex system (Fig. S1 and S2, ESI†)—with sometimes subtle interdependences—are determined by the absolute and/or relative rate coefficients not only of the 1,6-H shifts, but of several other processes such as the O_2 additions and -eliminations, all of which have to await (more accurate) experimental determination.

To summarize, we acknowledge that both the small overestimation of the predicted HPALD yield (37%) in comparison with the experiment-based yield in the experiment of Paulot *et al.* (25%, see above) and the underestimation of the MVK and MACR yield compared with the experiments of

Karl *et al.* suggest that our adopted $k(1,6\text{-H})$ could be overestimated by about a factor of 2. Nevertheless, in absence so far of experimental $k(1,6\text{-H})$ data, and noting that these discrepancies could be (partly) due to uncertainties for other key reaction rates, we will in our modelling sections below adhere to the here adopted geometric average of the original first-principles values¹ for the $k(1,6\text{-H})$ rate coefficients, on the grounds that both the predicted global average HPALDs yield and the yield in high-isoprene-emission areas as in the GABRIEL campaign would decrease by only 10 to 15% (relative) upon halving $k(1,6\text{-H})$.²⁷

Formation of HO₂ and hydroperoxy-methyl-butenals (HPALDs)

Of much importance for the issues at hand are also the preliminary results recently presented by Dillon *et al.* indicating that HO₂ is indeed produced at near-unity yields following OH-initiated oxidation of isoprene in clean air.²⁸

Such direct HO₂ generation supports the evidence discussed in the previous subsections, making together a strong case not only for our predicted 1,6-H shifts forming HO₂ + HPALDs in high yields, but also for very rapid removal of the HPALDs as evidenced by their low observed concentration.²⁴ Indeed, HPALDs were detected only by Paulot *et al.*, but not in any earlier photoreactor- or field study at low to moderate NO.^{20,23} The low concentration *versus* high formation rate of HPALDs can only be reconciled by their rapid removal, about an order of magnitude faster than possible by reaction with OH, and therefore only attributable to very fast photolysis, as we have hypothesised earlier.¹

Fast photolysis of 4-hydroperoxy-3/2-methyl-but-2-enals (HPALDs) and subsequent chemistry

The above is consistent with fast photolysis of the HPALDs of interest, O=CH-C(CH₃)=CH-CH₂O-OH and O=CH-CH=C(CH₃)-CH₂O-OH, at rates in the $J = 10^{-4}$ to 10^{-3} s^{-1} range. However, such rates are two orders of magnitude higher than the known J values for the two separate chromophore-moieties that constitute the HPALDs. On one hand, the conjugated α,β -enone (bi-)chromophore O=C-C=C-, as in MACR and MVK, exhibits a fair near-UV absorption cross section maximizing at $7.2 \times 10^{-20} \text{ cm}^2$ near 330 nm, but its *ca.* 8 kcal mol⁻¹ stronger =C-C= bond than in saturated aldehydes depresses for instance the quantum yield for MACR drastically to only 0.004, resulting in very low J values of the order of $2.5 \times 10^{-6} \text{ s}^{-1}$.²⁹ The -O-OH chromophore on the other hand suffers from a very low absorption cross section in the atmospherically relevant wavelength range, *e.g.* $\sigma = 1.0 \times 10^{-21} \text{ cm}^2$ at 325 nm, because *vertical* excitation of ground-state RO-OH to the repulsive RO-OH state requires *ca.* 140 kcal mol⁻¹ corresponding to ~ 200 nm photons,¹⁷ which keeps the atmospheric J down likewise to a few times 10^{-6} s^{-1} , notwithstanding the very weak hydroperoxide O-OH bond.

Therefore, the question of both fundamental and practical interest must be addressed as to the particular photochemical mechanism that can cause such a remarkably efficient synergy of the two separated moieties and result in O-OH bond

scission with near-unity quantum yield upon absorption of 290–370 nm photons by the α,β -enone group. A second issue is the energy content of the oxy co-product radical upon O-OH scission, which can have major repercussions on the subsequent chemistry. A high-level theoretical study of HPALD photodissociation is far beyond the scope of the present work, and in any case the errors that can currently be expected on computed energies of excited singlet states of the large structures involved here are of order of 5 or 10 kcal mol⁻¹ (see for example the differences between the various levels of theory for the computed vertical excitation energy of even the simplest α,β -enone, acrolein³⁰). Instead, we intend to provide semi-quantitative answers to the questions above—but sufficiently reliable to make our case, by making use of existing knowledge and available data. The results should also be useful to inform and guide experimentalists, who obviously must provide the final quantitative answers on the HPALD photolysis rate and on the nature of its products.

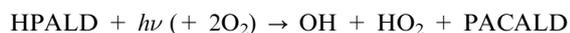
In the previous communication we suggested that 290–370 nm (n_1,π^*) excitation of the O=C-C=C- chromophore to its singlet S₁ state could be followed by fast internal conversion to the singlet ground state S₀[†] with a high vibration energy of about 90 kcal mol⁻¹, resulting in prompt homolysis of the weak O-OH bond at a rate of a few times 10^9 s^{-1} , *i.e.* (just) outrunning collisional relaxation. This suggestion implicitly assumed that internal conversion S₁ → S₀[†] is the fastest relaxation process of the S₁ state. However, we came to the insight that specifically for these molecules, another much faster S₁ process can occur that moreover should result directly in O-OH dissociation: *i.e.*, avoided crossing of the S₁ excited singlet state with the repulsive S₂ state of the other chromophore. Indeed, the S₁ excited surface of the O=C-C=C- chromophore must necessarily “cross” along the O-OH coordinate with the purely repulsive (n_2,σ^*)-excited S₂ surface of the -CH₂O-OH chromophore, a crossing that upon lifting the C_s symmetry restriction becomes avoided and so results in a low-lying transition state for direct dissociation to ground state OH and oxy radical, on the “new”, lower S₁/S₂ excited singlet surface. Here, we put forward this new mechanism, schematically represented in Fig. S7 of the ESI[†], as fastest and most efficient HPALD photolysis route.

In order to estimate the energy of the “crossing” point of the (n_1,π^*)-excited S₁ state of the α,β -enone and the repulsive (n_2,σ^*)-excited S₂ surface of the -CH₂O-OH chromophore, one needs to know (a) the excitation energy of the O=C-C=C- chromophore, (b) the evolution of the potential energy of the HPALD molecule in its S₁ state as a function of the O-OH distance—of which the shape should be identical to that in the ground state—and (c) the energy of the lowest (repulsive) excited state (S₂) of the -CH₂O-OH moiety also as a function of the O-OH distance. These data are available: the adiabatic excitation energy (a) was experimentally determined for acrolein by Walsh at 74 kcal mol⁻¹,³¹ while (b) and (c) can both be taken from the recent high-level computations by Watts and Francisco³² for CH₃O-OH, in combination with the vibration zero point energy (VZPE) data from Sun *et al.*³³ Note that RO-OH hydroperoxide dissociation energies for allylic R—such as for the HPALDs—have been shown quasi identical to those for R = (any) alkyl,³⁴ with the most recent

experimental determination of $D_e(\text{CH}_3\text{O}-\text{OH})$, supported by high-level *ab initio* values, yielding $42.6 \pm 0.6 \text{ kcal mol}^{-1}$.³⁵ On this basis, as detailed *in extenso* in the ESI†, the energy barrier for O–OH homolysis on the symmetry-free excited singlet surface is estimated at less than 10 kcal mol^{-1} . The nascent S_1^\dagger state as formed over most of the (n_1, π^*) absorption band should therefore have enough excess vibration energy to promptly dissociate in this way, at RRKM-estimated rates in the range 10^{10} – 10^{12} s^{-1} , *i.e.* faster than collisional relaxation of S_1^\dagger or $S_1 \rightarrow T_1$ intersystem crossing or $S_1 \rightarrow S_0$ internal conversion. For the particular HPALD-specific photolysis mechanism newly proposed here, a quantum yield approaching unity in atmospheric conditions is therefore expected. Adopting the $\sigma(\lambda)$ of MACR,¹⁷ one can so estimate an average daytime $J(\text{HPALD})$ close to $5 \times 10^{-4} \text{ s}^{-1}$ for the spectral flux conditions of the GABRIEL campaign.

An alternative mechanism *via* a 1,5-H shift of the hydroperoxide- α -H to the carbonyl-O in the S_1 biradical, followed by spontaneous OH expulsion from the unstable³⁶ $-\text{C}^\bullet\text{HO}-\text{OH}$ moiety, is entropically strongly disadvantaged and estimated to be slower despite its probably lower barrier.

The $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{O}^\bullet$ co-product of the direct O–OH dissociation above will undergo a fast 1,5-H shift of the aldehyde-H to the oxy-O to form $\text{O}=\text{C}^\bullet-\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ (see ESI†). As detailed in the ESI†, the nascent acyl radical will be slightly activated, but insufficient for prompt elimination of the CO to outrun collisional stabilization. Note that for the photolysis mechanism we first suggested,¹ *i.e.* *via* $S_1 \rightarrow S_0^\dagger$ internal conversion and subsequent O–OH homolysis of the highly activated S_0^\dagger , the subsequent acyl radical would contain 55–60 kcal mol^{-1} internal energy and therefore promptly eliminate the CO (see ESI†), thus giving rise to a very different subsequent chemistry. For the HPALD photolysis mechanism proposed here, the thermalized acyl radical will add O_2 to form $^\bullet\text{OO}-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$, a radical that is quasi-identical to the isoprene Z- δ -OH-peroxys and, given the even stronger OO–H bond in peroxy-acids than in hydroperoxides,³⁷ should undergo a 1,6-H shift as *sub* (iii) with $k(298 \text{ K}) \geq 1 \text{ s}^{-1}$ (see ESI†), easily outrunning the traditional HO_2 and NO_x reactions at low- to moderate NO_x levels. Fast reaction of the resulting α -OH-alkoxy radical with O_2 yields $\text{HO}_2 + \text{HOO}-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CHCH}=\text{O}$ (4-oxo-2-methyl-but-2-en-oic peroxyacid), a peroxy-acid-aldehyde denoted here as PACALD (as also its 3-methyl analogue resulting from the initial 4-OH adducts of isoprene). Overall, HPALDs photolysis should therefore yield:



As detailed in the ESI† the competing HPALDs + OH reactions proceed through several channels that mostly regenerate OH, with estimated total rate coefficient $\approx 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (298 K), this estimate being based mainly on measured rate- and products data for analogous OH reactions with unsaturated carbonyls.^{17,38}

Importantly, the PACALDs, with O–OH bond even somewhat weaker than in HPALDs,³⁷ are expected to photodissociate *via* a similar mechanism as the HPALDs, but about twice as fast, as they feature a doubly conjugated

$\text{O}=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ chromophore with ~ 1.5 times higher maximum σ_{max} that is moreover shifted to a longer λ_{max} of $\sim 345 \text{ nm}$.³⁹



with estimated $J(\text{PACALD}) \approx 10^{-3} \text{ s}^{-1}$ for daytime GABRIEL conditions (see the ESI†). The co-product radical should promptly eliminate CO_2 and then add O_2 to form $^\bullet\text{OO}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{O}$. The fate of this peroxy still needs closer examination; as argued in the ESI†, it could yield a third OH radical. The PACALDs + OH reactions, on the other hand, are expected to be negligibly slow (see ESI†) compared to photolysis. Note again that, as we now recognized (see ESI†), the tentative HPALD photolysis mechanism suggested at first¹ cannot yield the photolabile PACALDs.

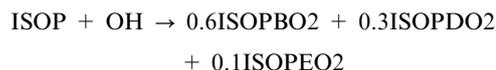
We must also emphasize the major impact on the overall OH budget of the subsequent chemistry of the oxy-radical formed in the particular HPALD photolysis mechanism proposed here, because of its potential to generate ample additional OH—as opposed to traditional chemistry of this oxy resulting in compounds that will instead consume OH.

Thus, the proposed 1,6-H shift isomerisation of the isoprene Z- δ -OH peroxy radicals and fast photolysis of the resulting HPALDs with subsequent photochemistry that can yield overall 2 or even 3 OH radicals, constitute together a viable and soundly based mechanism that can rationalize the major, unexpected OH-regeneration observed in areas dominated by isoprene oxidation.

Global impact of newly proposed chemistry

Implementation in a global chemistry-transport model (CTM)

The newly proposed reactions have been implemented in a reduced form in a global chemistry-transport model of the troposphere, the Intermediate Model for the Annual and Global Evolution of Species (IMAGESv2).⁴⁰ The various OH-adducts and hydroxy-peroxy radicals generated in the oxidation of isoprene by OH are replaced by a much simpler system involving only three peroxy radicals:



where ISOPBO2 and ISOPDO2 represent the peroxys formed through the addition of OH to carbons 1 and 4, respectively, and ISOPEO2 represents the peroxys formed through the minor remaining additions. Note that the δ -OH-peroxys are not represented explicitly. Their traditional reaction products (*e.g.* HALDs) can be neglected, as they are formed at yields of at most a few percents in most atmospheric conditions (see Fig. 1). ISOPBO2 and ISOPDO2 undergo unimolecular reactions accounting for the 1,5- and 1,6-H shifts of the isoprene-peroxys:



The rates of these reactions were optimized so that the simplified scheme reproduces the key product yields (for HPALD, HO₂ and OH) of the full reaction set to better than 1% at 293 and 303 K in the relevant atmospheric range (<400 ppt NO). The reason why reactions of specific isomers/conformers in a given pool of peroxy radicals (say ISOPBO2) can be attributed to the entire pool in a kinetically meaningful way, is the near-equilibrium population of the various isomers/conformers in the specified conditions (see above); the overall rate coefficients above thus represent the peroxy isomer/conformer-specific $k(1,6\text{-H})(T)$ or $k(1,5\text{-H})(T)$ multiplied by the respective equilibrium population fractions.

We rely on MIM2⁴¹ for the reaction mechanism following the reactions of ISOPBO2 and ISOPDO2 with NO and HO₂, except that we include the formation of isoprene-epoxides (IEPOX) in the OH-reaction of the hydroperoxides ISOPBOOH and ISOPDOOH,²⁴ as well as the further degradation of IEPOX by OH. The OH-reaction of ISOPEOOH (formed from ISOPEO2 + HO₂) does not lead to epoxides formation, but is assumed to form HCOC5 + OH (HCOC5 is a C5-hydroxy carbonyl in MIM2). Note that MIM2 includes radical propagating channels for the reactions of HO₂ with acyl peroxy radicals (with a 50% channel ratio) and β-oxo peroxy radicals (15% channel ratio).

The cross-reactions of the isoprene peroxy radicals are included explicitly. The self-reaction rates are based on laboratory data for similar β-hydroxy peroxy radicals:^{42,43}

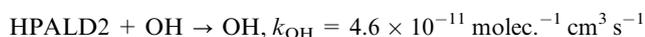
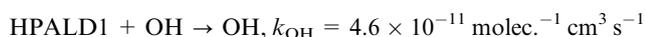
$$k_{\text{self}}(\text{ISOPBO2}) = 7 \times 10^{-14} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_{\text{self}}(\text{ISOPDO2}) = 6 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_{\text{self}}(\text{ISOPEO2}) = 5 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

The rates for the reactions of two different peroxy radicals A and B are calculated with $k(A + B) = 2 \times (k_{\text{self}}(A) \times k_{\text{self}}(B))^{1/2}$. The branching ratios of the possible reaction channels are obtained from ref. 44.

The further photooxidation of the HPALDs, already addressed above and in the ESI†, remains to be confirmed and fully elucidated. However, since both their OH-oxidation and photolysis are expected to (re-)generate OH radicals, we synthesize their possible effect with



where OVOCs is a mix of typical isoprene oxidation products very likely to be produced in the photooxidation of the HPALDs: OVOC = 0.5 CH₂(OH)COCH₃ + 0.5 CH₃COCHO + 0.25 CH₂(OH)CHO + 0.25 CHOCHO + CH₂O. The stoichiometric coefficients of the products are arbitrary, except for carbon balance. Different values of *m* will be tested (1 and 3), which should be considered as likely lower and upper bounds to the overall generation of OH due to the photolysis of

HPALDs. The HPALD photolysis rate is calculated using the absorption cross section of methacrolein,¹⁷ with a quantum yield of 1 (see above).

The global CTM simulations are performed at a spatial resolution of 2°(latitude) × 2.5°(longitude) and for the year 2005, with a 4-month spin-up time starting on Sep. 1 in the preceding year. Meteorological fields are obtained from ECMWF operational analyses. Isoprene emissions are estimated using the MEGAN algorithm with ECMWF meteorological fields.⁴⁵ Global isoprene emissions amounted to 450 Tg in 2005.

Global modeling results

Three modeling experiments were conducted. The isomerizations of isoprene peroxy radicals are ignored in run A, whereas they are included in runs B and C. The photolysis of HPALD is assumed to generate one HO₂ and either 1 (run B) or 3 (run C) OH radicals.

The globally averaged HPALD yield from isoprene is estimated to be 60% in both run B and run C. The HPALD yield exceeds 50% in most regions, even at mid-latitudes (Fig. 2).

The lowest yields are calculated over cool and polluted areas characterized by high NO abundances, such as Northwestern Europe, as expected from the NO- and temperature dependence of the primary yields (Fig. 1). The globally averaged yield of MACR + MVK from the OH-initiated oxidation of isoprene is estimated to be about 20%, with equal contributions from the 1,5-H-shift of the β-OH-peroxys and the traditional reactions of these peroxys with NO and RO₂. The average yield of isoprene hydroperoxides is estimated to be 18%, of which about half is oxidized to epoxides.

The very short atmospheric lifetime of the major products HPALDs (*e.g.* ~25 minutes in the conditions of the GABRIEL campaign), possibly explains why these particular compounds have not been speciated and reported in atmospheric conditions, though they should have been included in total observed hydroperoxides or aldehydes. The concentrations of key compounds observed in the planetary boundary layer (PBL) during the GABRIEL campaign⁴

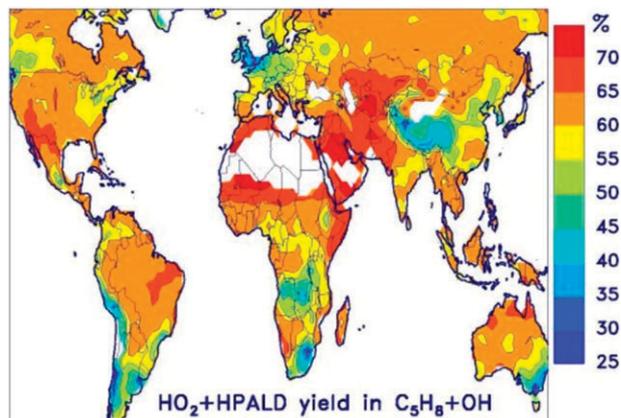


Fig. 2 Column-averaged primary yield of HO₂ and HPALD in the oxidation of isoprene by OH (July 2005), calculated with the IMAGESv2 CTM (run C, see ESI† for details).

Table 1 Observed and modelled concentrations of key compounds in the PBL during the GABRIEL campaign. Model results are concentration averages below 1.5 km height, between 9–17 LT

	Obs.	Run A	Run B	Run C
NO (pptv)	20	26	21	17
OH (10^6 cm^{-3})	5.6	1.5	2.8	4.2
HO ₂ (10^8 cm^{-3})	10.5	3.3	6.8	7.7
Isoprene (ppbv)	2.0	2.7	1.9	1.3
O ₃ (ppbv)	18.5	17	17	17

conducted in the Amazon Basin in October 2005 are compared with the model results in Table 1.

The isomerization of isoprene peroxys is found to strongly enhance OH levels in this remote, isoprene-rich environment, by factors of about 2 and 3 in runs B and C, respectively. Run C, which includes a large HO_x regeneration in the further photolysis mechanism of HPALDs, performs very well against the GABRIEL observations, with only a slight underestimation (<30%) for both OH and HO₂, contrasting with the underestimation by factors 3–4 in run A.

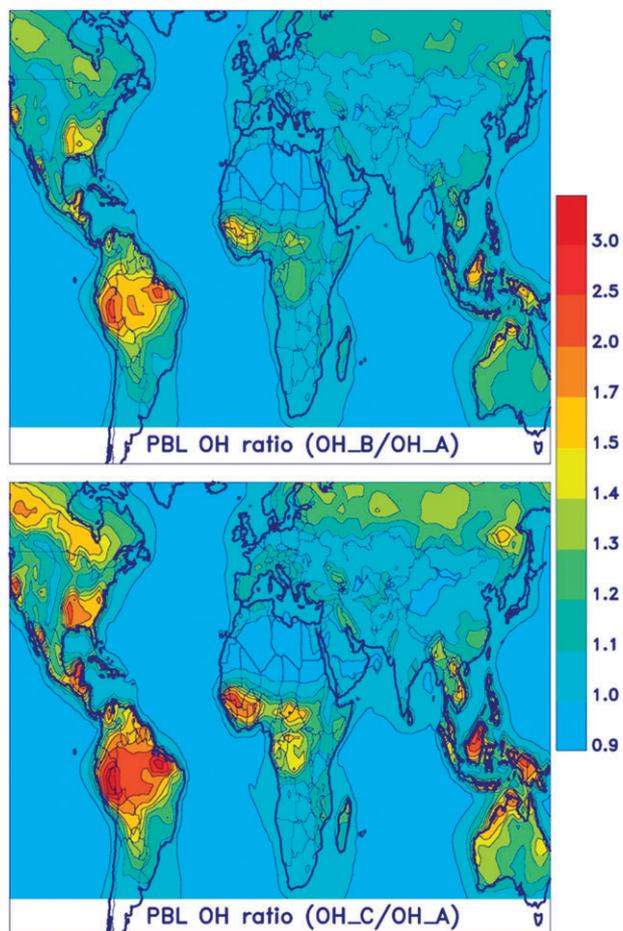


Fig. 3 Calculated ratio of the OH concentration in the planetary boundary layer (PBL) between simulations B (upper panel) or C (lower panel) and the simulation A which ignores the isomerization reactions of isoprene peroxy radicals, for the month of July. Simulations B and C differ by the assumed extent of OH regeneration in the photodegradation of the HPALDs (see text). The PBL extends to an altitude of about 1.5 km.

Note that halving the $k(1,6\text{-H})$ (see above) reduces the modeled OH and HO₂ levels for run C by only $\sim 10\%$,²⁷ in agreement with the highly non-linear HPALD response discussed above. Note also that a perfect agreement of the model with these observations cannot be expected, since many poorly represented processes (e.g. emission of other VOCs, meteorology, etc.) might affect the ability of the model to reproduce the measurements at this location.

The estimated HO_x enhancements in Table 1 are significantly larger than in a recent study using the global model STOCHEM,¹⁴ since the combined effect of the isomerization reactions as well as of other mechanism updates was found by Archibald *et al.* to enhance the simulated HO_x concentrations by (only) about 35% in the GABRIEL campaign area. This lower sensitivity compared to our results is partly due to the overestimated NO_x (500 pptv) and O₃ (45 ppbv) mixing ratios calculated by STOCHEM over Amazonia. It is also related to the photooxidation of the HPALDs: their photolysis was assumed to generate one OH radical along with a peroxy radical in the STOCHEM simulations, as opposed to one HO₂ and either 1 or 3 OH radicals in our simulations. Moreover, in our model, OH-oxidation of the HPALDs regenerates OH (see ESI†).

Fig. 3 shows the impact of the new chemistry (runs B or C vs. A) on OH concentrations in the PBL. The PBL-averaged OH levels are increased by factors of more than 1.5–2 over the Southeastern United States and over Tropical forests when the new chemistry is included (run B). The increase is even larger (factor 1.7–3) when the photolysis of HPALDs regenerates OH efficiently (run C). At the first model level (about 10 m above the surface), the OH increases reach factors of 2–3 in run B, and up to 7 in run C.

Conclusions

In this paper, some (implicit) criticisms in the literature on our newly proposed isoprene oxidation chemistry¹ were addressed, while altogether a body of recent experimental evidence could be construed in support of our mechanism, though chamber and field observations required minor modifications of some of the rate coefficients, within the uncertainties of the original first-principles values¹ and without marked impact on the HO_x regeneration yields.

Recently reported measurements allow us to further narrow down the uncertainty range of the crucial $k(1,6\text{-H})$ rate coefficient (averaged) to *ca.* 0.3–1.3 times the value we adopted in this work, *i.e.* about $2_{-1.2}^{+1.4} \text{ s}^{-1}$ at 303 K or $\sim 8_{-5}^{+6} \times 10^8 \times \exp(-6000/T) \text{ s}^{-1}$ for $T = 280\text{--}320 \text{ K}$, though this must await confirmation by direct experiment. A particular photochemical mechanism is newly put forward for the crucial photolysis of the hydroperoxy-methyl-butenals (HPALDs) that rationalizes its unusually high quantum yield. The high potential impact on the OH concentration over large continental areas is amply demonstrated. Clearly, much work still remains to be done on refining the mechanism and improving the accuracy of the rate coefficients. Yet, first and foremost, there is an urgent need for experimental confirmation and accurate quantification of the formation of the HPALDs (and PACALDs) intermediates, and of their OH-regenerating photolysis.

Acknowledgements

This research was carried out in the frame of the BELSPO SSD project "IBOOT" (contract SD/AT/03), with additional support by FWO-Flanders and KULeuven Research Council.

Notes and references

- J. Peeters, T. L. Nguyen and L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5935.
- D. Tan, *et al.*, *J. Geophys. Res.*, 2001, **106**, 24407.
- N. Carslaw, D. J. Creasey, D. Harrison, D. E. Heard, M. C. Hunter, P. J. Jacobs, M. E. Jenkin, J. D. Lee, A. C. Lewis, M. J. Pilling, S. M. Saunders and P. W. Seakins, *Atmos. Environ.*, 2001, **35**, 4725.
- J. Lelieveld, T. M. Butler, J. N. Crowley, T. J. Dillon, H. Fischer, L. Ganzeveld, H. Harder, M. G. Lawrence, M. Martinez, D. Taraborrelli and J. Williams, *Nature*, 2008, **452**, 737, and references therein.
- T. M. Butler, D. Taraborrelli, C. Brühl, H. Fischer, H. Harder, M. Martinez, J. Williams, M. G. Lawrence and J. Lelieveld, *Atmos. Chem. Phys.*, 2008, **8**, 4529, and references therein.
- A. Hofzumahaus, *et al.*, *Science*, 2009, **324**, 1702.
- X. Ren, *et al.*, *J. Geophys. Res.*, 2008, **113**, D05310.
- T. A. M. Pugh, A. R. MacKenzie, C. N. Hewitt, B. Langford, P. M. Edwards, K. L. Furneaux, D. E. Heard, J. R. Hopkins, C. E. Jones, A. Karunaharan, J. Lee, G. Mills, P. Misztal, S. Moller, P. S. Monks and L. K. Whalley, *Atmos. Chem. Phys.*, 2010, **10**, 279.
- A. Guenther, *et al.*, *J. Geophys. Res.*, 1995, **100**, 8873.
- (a) J. Peeters, W. Boullart and J. Van Hoeymissen, in *Proceedings of Eurotrac Symposium '94*, ed. P. M. Borrell, *et al.*, SPB Academic Publishers, The Hague, 1994, p. 110; (b) J. Peeters, W. Boullart, V. Pultau, S. Vandenberg and L. Vereecken, *J. Phys. Chem. A*, 2007, **111**, 1618.
- J. Park, C. G. Jongsma, R. Zhang and S. W. North, *J. Phys. Chem. A*, 2004, **108**, 10688, and references therein.
- G. da Silva, C. Graham and Z.-F. Wang, *Environ. Sci. Technol.*, 2010, **44**, 250.
- O. Perrin, A. Heiss, F. Doumenc and K. Sahetchian, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2323.
- A. T. Archibald, M. C. Cooke, S. R. Uttember, D. E. Shallcross, R. G. Derwent and M. E. Jenkin, *Atmos. Chem. Phys. Discuss.*, 2010, **10**, 5863.
- Anonymous Referee, *Atmos. Chem. Phys. Discuss.*, 2010, **10**, C1966-C1966. <http://www.atmos-chem-phys-discuss.net/10/C1966/2010/acpd-10-C1966-2010.pdf>.
- B. Ghosh, A. Bugarin, B. T. Connell and S. W. North, *J. Phys. Chem. A*, 2010, **114**, 2553.
- IUPAC subcommittee for Gas Kinetic Data Evaluation, <http://www.iupac-kinetic.ch.cam.ac.uk/>; and references therein.
- J. Zhao, R. Y. Zhang and S. W. North, *Chem. Phys. Lett.*, 2003, **369**, 204.
- T. S. Dibble, *J. Phys. Chem. A*, 2002, **106**, 6643.
- M. Karl, H.-P. Dorn, F. Holland, R. Koppmann, D. Poppe, L. Rubb, A. Schaub and A. Wahner, *J. Atmos. Chem.*, 2006, **55**, 167.
- U. R. Pöschl, R. von Kuhlmann, N. Poisson and P. J. Crutzen, *J. Atmos. Chem.*, 2000, **37**, 29.
- H. Geiger, I. Barnes, I. Bejan, T. Benter and M. Spittler, *Atmos. Environ.*, 2003, **37**, 1503.
- T. Karl, A. Guenther, A. Turnipseed, G. S. Tyndall, P. Artaxo and S. Martin, *Atmos. Chem. Phys.*, 2009, **9**, 7753.
- F. Paulot, J. D. Crouse, H. G. Kjaergaard, A. Kurten, J. M. St. Clair, J. H. Seinfeld and P. O. Wennberg, *Science*, 2009, **325**, 730.
- A. A. Boyd, P.-M. Flaud, N. Daugey and R. Lesclaux, *J. Phys. Chem. A*, 2003, **107**, 818.
- E. E. Greenwald, B. Ghosh, K. C. Anderson, K. S. Dooley, P. Zou, T. Selby, D. L. Osborn, G. Meloni, C. A. Taatjes, F. Goulay and S. W. North, *J. Phys. Chem. A*, 2010, **114**, 904.
- J. Stavrakou, J. Peeters and J. F. Müller, *Atmos. Chem. Phys. Discuss.*, 2010, **10**, 16551.
- T. J. Dillon, J. N. Crowley, H. Harder, D. Kubistin and M. Martinez-Harder, *Experimental evidence for HO₂ production from OH + isoprene in clean air*, Book of Abstracts, 21st International Symposium on Gas Kinetics, KULeuven, Leuven, 2010, p. 186.
- P. G. Pinho, C. A. Pio and M. E. Jenkin, *Atmos. Environ.*, 2005, **39**, 1303.
- O. S. Bokareva, V. A. Bataev, V. I. Pupyshev and I. A. Godunov, *Spectrochim. Acta, Part A*, 2009, **73**, 654.
- A. D. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498.
- J. D. Watts and J. S. Francisco, *J. Chem. Phys.*, 2006, **125**, 104301.
- H. Sun, C.-J. Chen and J. W. Bozzelli, *J. Phys. Chem. A*, 2000, **104**, 8270.
- N. Sebbar, H. Bockhorn and J. W. Bozzelli, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3691.
- J. Matthews, A. Sinha and J. S. Francisco, *J. Chem. Phys.*, 2005, **122**, 221101.
- L. Vereecken, T. L. Nguyen, I. Hermans and J. Peeters, *Chem. Phys. Lett.*, 2004, **393**, 432.
- Y.-R. Luo, *Bond dissociation energies in organic compounds*, CRC Press, Boca Raton, 2003, and references therein.
- (a) J. J. Orlando and G. S. Tyndall, *J. Phys. Chem. A*, 2002, **106**, 12252; (b) J. J. Orlando, G. S. Tyndall and S. E. Paulson, *Geophys. Res. Lett.*, 1999, **26**, 2191.
- M. P. O'Connor, J. C. Wenger, A. Mellouki, K. Wirtz and A. Munoz, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5236.
- T. Stavrakou, *et al.*, *Atmos. Chem. Phys.*, 2009, **9**, 8341; T. Stavrakou, *et al.*, *Atmos. Chem. Phys.*, 2009, **9**, 1037.
- D. Taraborrelli, M. G. Lawrence, T. M. Butler, R. Sander and J. Lelieveld, *Atmos. Chem. Phys.*, 2009, **9**, 2751.
- M. E. Jenkin, A. A. Boyd and R. Lesclaux, *J. Atmos. Chem.*, 1998, **29**, 267.
- A. A. Boyd, R. Lesclaux, M. E. Jenkin and T. J. Wallington, *J. Phys. Chem.*, 1996, **100**, 6594.
- M. Capouet, J. Peeters, B. Nozière and J.-F. Müller, *Atmos. Chem. Phys.*, 2004, **4**, 2285-2311.
- J.-F. Müller, *et al.*, *Atmos. Chem. Phys.*, 2008, **8**, 1329.