



A detailed case study of isoprene chemistry during the EASE96 Mace Head campaign

N. Carslaw*, N. Bell, A.C. Lewis, J.B. McQuaid, M.J. Pilling

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

Received 13 August 1999; received in revised form 10 December 1999; accepted 20 December 1999

Abstract

A detailed chemical mechanism has been used in conjunction with high-quality field measurements in order to assess the potential role of isoprene at a clean coastal Northern Hemisphere site. The importance of isoprene as a source of peroxy radicals, formaldehyde and ozone is discussed in some detail for a case study day (July 17 1996). Between 10:00 and 16:00 h GMT, isoprene accounts on average for 15% of the OH removal, yet is responsible for the production of about 30% of the HO₂ radicals. Isoprene is also responsible for between 40 and 60% of the HCHO formation, and 20–40% of the 2 ppb h⁻¹ conversion of NO to NO₂ by peroxy radicals. We discuss the significant time lag between HCHO formation and destruction, a time lag that must be accounted for in order to accurately calculate the rate of HO₂ production from isoprene degradation, and the implications of the isoprene oxidation for atmospheric chemistry. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidation; Peroxy radicals; Ozone; Formaldehyde; Box model

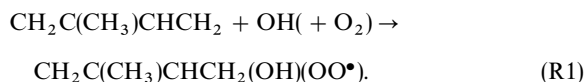
1. Introduction

Carslaw et al. (1999a) recently described a new technique for model construction, based on a tailored chemical mechanism combining field measurements and a detailed chemical scheme. The resulting model was used to predict radical concentrations for comparisons with measurements made during the Eastern Atlantic Summer Experiment 1996 (EASE96) campaign at the Mace Head Atmospheric Observatory, a remote site on the west coast of Ireland. The model uses an explicit chemical mechanism and consequently, it is possible to study the detailed chemistry of intermediates in the overall oxidation. In this paper, the chemistry of isoprene (2-methyl-1,3-butadiene, CH₂=C(CH₃)-CH=CH₂) is investigated.

Isoprene is a biogenic hydrocarbon emitted from vegetation, including some varieties of oak and spruce trees,

bracken and common gorse (Hewitt and Street, 1992), and its emission is both temperature and light intensity dependent (Fehsenfeld et al., 1992). Isoprene has been estimated to constitute 44% of the estimated annual global VOC flux of 1150 Tg C from natural sources (Guenther et al., 1995). Once emitted, the main fate of isoprene is to react with the OH radical, and to a lesser extent, with O₃ and the nitrate (NO₃) radical. In common with many other biogenic species, isoprene is extremely reactive and has a typical atmospheric lifetime of tens of minutes. For instance, for a hydroxyl radical (OH) concentration of 5 × 10⁶ molecules cm⁻³, the lifetime of isoprene is about 30 min.

The chemistry of isoprene has been reasonably well studied (Fehsenfeld et al., 1992; Carter and Atkinson, 1996). Attack by OH proceeds via addition:



Six peroxy radical isomers are formed in R1 but the overall reaction can be adequately represented by including only the four major isomers:

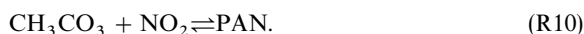
* Corresponding author.

E-mail address: nicolas@chem.leeds.ac.uk (N. Carslaw).

Table 1
% loss of OH from measured hydrocarbons and CO on 17 July 1996

Species	10:00	11:00	12:00	12:30	13:00	14:00	15:00	16:00	Average
Carbon monoxide	37.6	31.2	24.5	23.5	23.1	24.9	27.8	31.0	28.0
Methane	11.7	8.7	7.9	7.4	7.2	7.7	8.1	8.6	8.4
Ethane	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Ethene	0.2	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.3
Propane	0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.3
Propene	0.4	1.2	1.1	1.0	0.9	0.9	0.8	0.7	0.9
<i>Cis-</i> and <i>trans</i> -2-Butene	0.7	2.5	2.2	2.0	1.9	1.7	1.7	1.7	1.8
Isoprene	10.0	17.9	23.1	23.1	22.6	14.1	6.8	2.8	15.1
1,3 Butadiene	0.2	0.8	0.7	0.6	0.6	0.6	0.6	0.6	0.6
1,3,5-trimethylbenzene	0.7	0.6	0.5	0.5	0.4	0.5	0.4	0.3	0.5
Toluene	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.4

In addition, the reaction of CH_3CO_3 with NO_2 can lead to the formation of PAN:



PAN acts as a temporary reservoir for NO_x ($\text{NO} + \text{NO}_2$) and peroxy radicals, releasing them at a temperature-dependent rate.

Horowitz et al. (1998) used a three-dimensional, continental-scale model of tropospheric O_3 – NO_x –NMHC chemistry over North America in summer. The authors found that by omitting isoprene from model runs, ozone concentrations decreased by up to 25 ppb, the concentration of PAN decreased by 40–60%, and OH concentrations increased by a factor of 2 or more, hence reducing NO_x concentrations (as more OH reacted with NO_2). In fact, the net export of NO_x and organic nitrates from the US continental boundary layer to the global atmosphere decreased by 22%. Similarly, export of PAN was reduced by 81%. The presence of isoprene, therefore, has an important effect on aspects of atmospheric chemistry. Control strategies would not reduce the contribution of biogenically produced isoprene to ozone production, and so it is essential that we try to understand the role isoprene plays in the atmosphere.

This case study investigates in detail 17 July from the 1996 Eastern Atlantic Summer Experiment (EASE96). Table 1 shows the % loss of OH due to measured hydrocarbons and CO on this day (using only the initial reaction of each species with OH and discounting reactions of secondary products at this stage). 17 July was selected for this case study owing to its relatively high concentrations of isoprene (up to 350 ppt), which contributed on average 15% of the OH loss due to CO, CH_4 and NMHC. Although an isoprene concentration of 350 ppt is low compared to studies carried out in Southern Europe (e.g. Staffelbach et al., 1997) and North America (e.g. Fehsenfeld et al., 1992; Biesenthal et al., 1998), it

can have a significant impact on a clean atmosphere site (Table 1). This paper addresses key aspects of isoprene chemistry at Mace Head on 17 July 1996.

2. Site description and experimental

The EASE96 campaign was held between 13 July and 5 August at the Mace Head Atmospheric Observatory ($53^\circ 19' 34'' \text{N}$, $9^\circ 54' 14'' \text{W}$). The campaign formed part of the OXidative Capacity of the Oceanic Atmosphere (OXICOA) component of the NERC funded Atmospheric Chemistry Studies of the Oceanic Environment (ACSOE) project. The station is situated on the remote west coast of Ireland, 60 km west of Galway, and is part of Advanced Global Atmospheric Gases Experiment (AGAGE), and is also a Tropospheric Ozone Research (EUROTRAC/TOR) station. A full description of the site can be found in Cvitas and Kley (1994).

The concentration of isoprene (and 27 other NMHC) was monitored hourly using an automated programmed temperature vapourisation (PTV) injector gas chromatograph-flame ionisation (GC-FID) system (Lewis et al., 1997). A PTV (OPTIC 400, Ai Cambridge Ltd., Cambridge, UK) injector liner is packed with an adsorbent material (~ 200 mg) and capped at either end with glass wool. The liner is placed inside the PTV injector and a combination of two 6 port valves are used to route samples of air over the adsorbent trap for sample preconcentration. Air was sampled via a 10 m glass manifold (Schott, Germany), with the residence time in the manifold in the region of 1–2 s. Peak identification and calibration were made by comparison with a standard 27 component mixture at the ppb level (NPL, Teddington, UK). A detection limit ($\text{SNR} = 2$) of better than 5 ppt was achieved for isoprene. Samples were collected between 13 July and 5 August 1996. A full discussion of the observed NMHC can be found in Lewis et al. (1997).

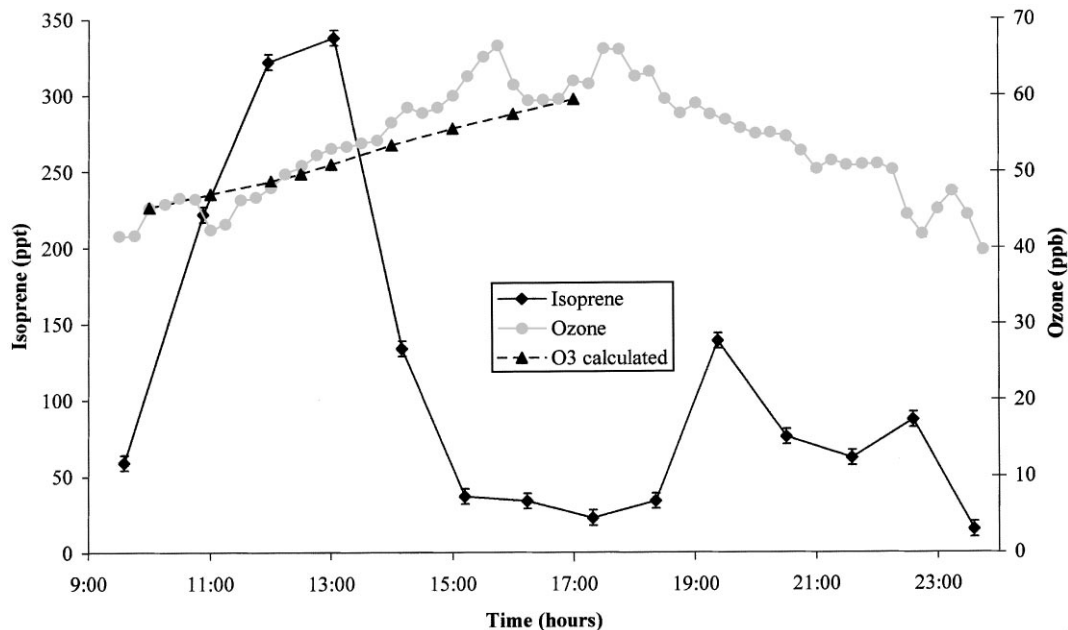


Fig. 2. Diurnal profiles of isoprene and uncertainty limits in ppt (black line with circles) and ozone in ppb (grey line with circles) measured at the Mace Head Atmospheric Station on 17 July 1996 during the EASE96 campaign. Also shown by the black dashed line with triangles is the O_3 concentration as predicted using the modelled NO to NO_2 conversions by peroxy radicals (see text).

Ozone was monitored by UV absorption (254 nm) using a commercially available API 400 ozone analyser (ETI Corp. UK), which was calibrated during the campaign using a traceable ozone source (National Physics Laboratory, UK). Other measurements used in the model are discussed by Carslaw et al. (1999a).

3. Model

The model has been described in detail previously (Carslaw et al., 1999a). Briefly, the zero-dimensional box model was constructed by considering the concentrations of NMHC measured during the EASE96 campaign. Between 94 and 98% of the OH loss due to CO and hydrocarbons could be accounted for by the following species: CO, CH_4 , ethane, ethene, propane, propene, isoprene, *cis*- and *trans*-2-butene, toluene, 1,3-butadiene, DMS and 1,3,5-trimethylbenzene. With the exception of the DMS mechanism from Yin et al. (1990a, b), the chemical mechanisms and rate coefficients for these species were taken from a Master Chemical Mechanism (MCM) devised by Jenkin et al. (1997) and used to construct a tailored chemical mechanism. The MCM is an explicit mechanism and does not contain empirical lumping, or surrogate species.

The model is constrained by observations of NO_2 , NO, O_3 , H_2 , CO, CH_4 , the 11 selected NMHC, HCHO, PAN, SO_2 , aerosol surface area, $j(O^1D)$, $j(NO_2)$, temper-

ature and relative humidity, and so emissions data are not required. Available data are averaged to 15 min model input points. The model also includes dry deposition terms and heterogeneous loss as detailed by Carslaw et al. (1999a). In total, there are 1666 reactions and 505 species, and the rate equations are integrated for 24 h using the FACSIMILE code (Curtis and Sweetenham, 1987).

The intermediate species in the model, for which no measured data are available (such as carbonyls), were initialised at zero at 0000 hours. Any errors introduced by this approach were checked by running the model again with the intermediate concentrations initialised at the values calculated at the end of the day. There was little difference in the modelled OH and HO_2 (< 3%). Poppe et al. (1994) concluded that complete exclusion of these species from their model led at most to a 20% difference in predicted OH concentrations.

4. Results and discussion

Fig. 2 shows the concentrations of isoprene and ozone on 17 July 1996 (note that all times discussed in this paper are GMT, local time – 1 h). The isoprene concentration reaches a maximum of ~350 ppt at around 13:00 h. Owing to its short lifetime, isoprene is unlikely to have travelled more than a few kilometres to reach the site, and has probably been emitted by local vegetation.

Table 2

HO₂ production from the isoprene scheme between 10:00 and 16:00 on 17 July 1996, expressed as 30 min averages centred on the time shown. The HO₂ production rates are in units of 10⁵ molecule cm⁻³ s⁻¹. The production rate from CO, the other major sink for OH, is shown for comparison purposes

	10:15	10:45	11:15	11:45	12:15	12:45	13:15	13:45	14:15	14:45	15:15	15:45
ISOPBO = > ^a	5.5	5.2	8.5	10.1	12.0	12.3	14.6	9.7	9.7	6.2	5.0	4.2
CH ₃ O + O ₂ ^b	3.8	2.8	4.0	5.4	7.0	7.5	10.8	9.4	12.2	9.0	7.8	7.8
HCHO + hv ^b	1.8	2.2	3.0	3.0	4.5	3.9	3.5	3.6	3.9	5.2	4.4	3.8
ISOPDO = > ^a	2.5	2.3	3.6	4.2	4.8	4.7	5.4	3.1	2.6	1.4	0.73	0.54
HCHO + OH ^b	1.8	1.6	2.2	2.2	3.2	2.6	2.7	2.6	3.4	4.2	4.1	3.9
ISOPAO = > ^a	1.6	1.5	2.3	2.7	3.1	3.0	3.4	2.0	1.6	0.88	0.46	0.34
MGLYOX + hv	0.38	0.44	0.53	0.66	0.85	1.1	1.4	1.6	1.7	1.8	1.8	1.8
ISOPCO = > ^a	0.82	0.76	1.2	1.4	1.6	1.6	1.8	1.0	0.85	0.46	0.24	0.18
HMVKAO = > ^a	0.44	0.34	0.53	0.67	0.86	1.0	1.4	1.2	1.6	1.2	1.3	1.2
MACRO = > ^a	0.45	0.36	0.56	0.71	0.90	1.0	1.3	1.2	1.4	1.0	1.0	0.86
Total isoprene	20.6	19.1	28.7	34.2	43.1	43.7	52.5	41.4	45.7	37.0	31.9	29.2
OH + CO	47.2	37.7	35.7	34.2	35.5	35.2	39.4	36.0	44.3	39.8	43.3	44.8

^a = > denotes a decomposition reaction.

^b Only the contribution from isoprene chemistry has been tabulated – see next section.

Fig. 2 also shows a significant increase in ozone after 11:00 h. Indeed, isoprene is believed to have a significant effect on ozone production on the case study day (Monks et al., 1999).

5. HO₂ production

The concentration of the sum of peroxy radicals on 17 July determined by a chemical amplifier peaked about an hour and a half after solar noon. The asymmetry with respect to solar noon was confirmed by modelled concentrations of both HO₂ and CH₃O₂ (Monks et al., 1999). To investigate the cause of the asymmetry, each HO₂-producing reaction in the model mechanism was tagged, to identify how much HO₂ each reaction produces. In addition, indirect HO₂ producing routes (such as HCHO) have been quantified in terms of their parent hydrocarbon. As demonstrated in Table 1, isoprene chemistry is at least 10 times more important than each of the other NMHC in the model and hence the following discussion focuses on isoprene chemistry.

Isoprene degrades to form many secondary products, which react to yield HO₂ (Fig. 1). Some secondary products are formed only from isoprene, and it is simple to identify the HO₂ production as being from isoprene chemistry. However, other products are common to the degradation of several hydrocarbons in the model and it is more complicated to assess the isoprene contribution to the formation of HO₂ via these products. For radical species (i.e. CH₃CO₃ and CH₃O₂), the contribution from isoprene to the HO₂ production of each of them is assumed to be equal to the fraction of the production of that radical that is due to isoprene. For non-radical

species (i.e. CH₃CHO and HCHO), the analytical procedure described for formaldehyde in the next section is adopted to calculate the isoprene contribution to the HO₂ production.

The HO₂ rate analysis has been carried out between 10:00 and 16:00 h, which covers the period when NO_x data were available, and the 10 most important reactions producing HO₂ are detailed in Table 2. Also included is the rate of the reaction between OH and CO for comparison. Isoprene chemistry is responsible for an average HO₂ production rate of about 500 ppt h⁻¹ between 10:00 and 16:00 h, compared with a total production rate (i.e. from all model species) of 1580 ppt h⁻¹ for the same period. Therefore, isoprene chemistry is responsible for about one third of HO₂ production under these conditions.

Fig. 3 shows a selection of the hourly averaged HO₂ production rates to demonstrate the different time dependencies that are observed. Fig. 3a shows ISOPBO, which is formed when one of the peroxy radicals created from the OH oxidation of isoprene reacts with NO (Fig. 1). Once formed, ISOPBO rapidly decomposes, leading to the production of HO₂ radicals. Therefore, the diurnal profile of ISOPBO derived HO₂ is similar to the diurnal profile of isoprene itself (Fig. 2).

Fig. 3b shows HMVKAO, another alkoxy radical, which is formed through the degradation of MVK (Fig. 1). The lifetime of MVK is around 2.5 h at midday, so that HO₂ production continues to increase in magnitude for much longer than with ISOPBO, only decreasing for the 15:30 average. Finally, HO₂ production from the photolysis of MGLYOX (from the oxidation of MVK, lifetime of about 1.5 h at midday) (Fig. 3c) continues to increase throughout this entire period, although levelling

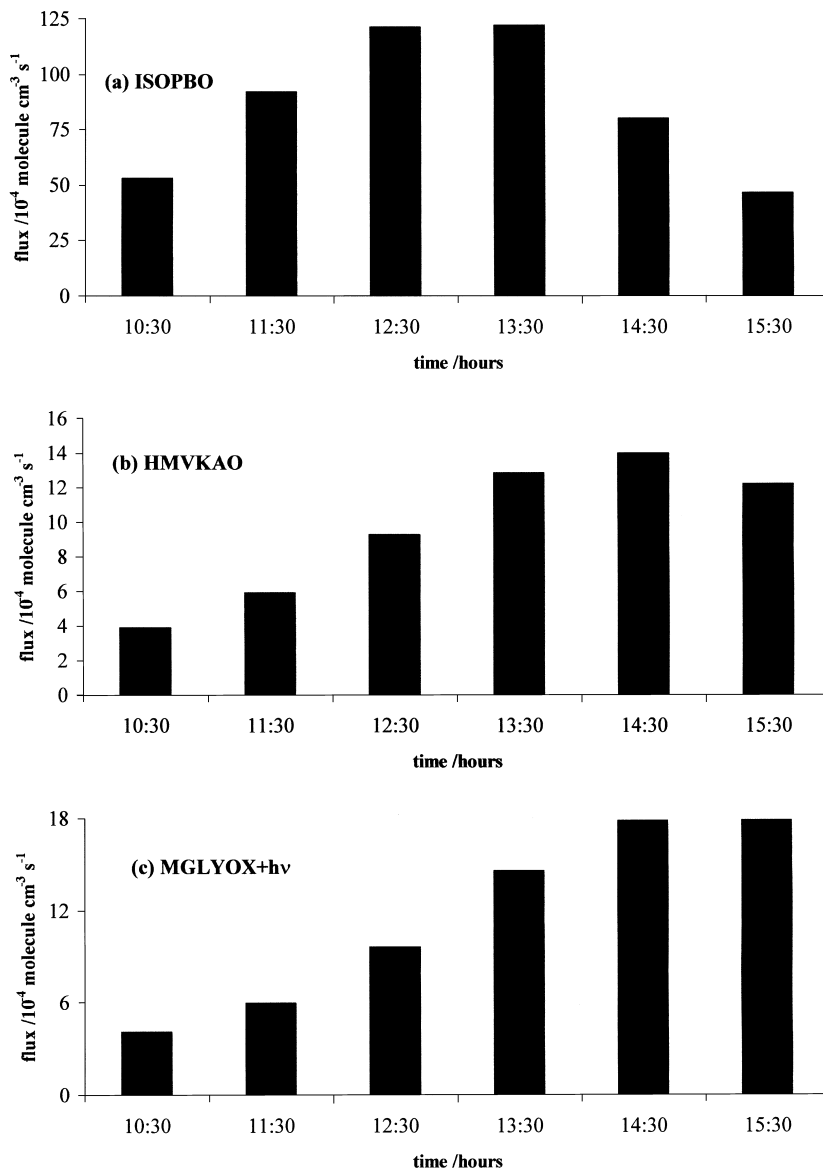


Fig. 3. Bar charts showing the hourly HO₂ production rates through various channels on 17 July 1996: (a) ISOPBO decomposition; (b) HMVKAO decomposition; and (c) MGLYOX + *hν*. Production rates are in units of 10⁴ molecule cm⁻³ s⁻¹.

off somewhat at the end. Note that these species derive from progressively further down the oxidation chain of isoprene (Fig. 1) and consequently, are important HO₂ producers at different times. Hence, we can begin to understand the observed asymmetry.

6. HCHO production

Fig. 1 demonstrates a number of HCHO formation routes from isoprene degradation by OH. HCHO then

produces HO₂ when it reacts with OH (R2) or undergoes photolysis (R3a). However, the lifetime of HCHO is long when compared to its production rate through R5 and R6. The rate-determining step in the production of HCHO is R5 where $k_5[\text{NO}] = 7.49 \times 10^{-3} \text{ s}^{-1}$, which is about 75 times faster than the inverse chemical lifetime of HCHO calculated at 12:00 hours ($\sim 1.00 \times 10^{-4} \text{ s}^{-1}$, lifetime $\sim 2.5 \text{ h}$). Therefore, in order to quantify the time dependence of HO₂ regeneration via formaldehyde (and other carbonyl species) produced from isoprene chemistry, it is necessary to take into

Table 3
Isoprene-derived contribution to HCHO production as % of total

	10:00	11:00	12:00	13:00	14:00	15:00	16:00
CH ₃ O + O ₂ ^a	9.3	10.4	13.1	16.3	18.4	16.8	17.9
HOCH ₂ CHO + hν ^a	0.4	0.5	0.7	1.0	1.3	1.6	1.5
HOCH ₂ CO ₃ + NO ^a	0.4	0.8	1.1	1.4	1.8	1.8	1.8
ISOPBO = > ^b	14.9	20.6	21.9	19.6	13.8	9.9	7.6
OH + OHCH ₂ C(CH=CH ₂)(CH ₃)ON(=O)=O	0.9	1.1	1.4	1.7	1.9	1.8	1.4
MVK + hν	0.8	1.0	1.4	1.6	1.7	1.8	1.5
HMVKAO = > ^b	1.1	1.3	1.7	2.1	2.4	2.6	2.2
ISOPDO = > ^b	6.7	8.7	8.6	6.9	3.4	1.4	1.0
MACO ₃ + NO	1.1	1.4	1.8	2.2	2.5	2.3	2.3
MACRO = > ^b	1.1	1.4	1.7	2.0	2.1	2.0	1.5
Total from isoprene chemistry	38.5	49.8	56.8	58.2	52.2	44.6	41.1

^aOnly the contribution from isoprene chemistry has been tabulated.

^b = > denotes a decomposition reaction.

account the effect of the time lag inherent in carbonyl decay.

In order to account for this time lag in HCHO decay, a convolution technique is used where the concentration of HCHO is determined from Eq. (1). In this manner, it is possible to ascertain the proportion of formaldehyde that is produced from isoprene products:

$$[\text{HCHO}](t) = [\text{HCHO}]_0 e^{-\int_0^t k_d(t) dt} + \int_0^t R(s) e^{-\int_s^t k_d(t) dt} ds, \quad (1)$$

where R is the time-dependent rate of production of HCHO from isoprene and is determined directly by integration of the model mechanism and $k_d(t)$ is the pseudo-first-order rate coefficient for reaction of HCHO ($k_d(t) = k_2[\text{OH}] + J_3$). The values of k_2 , $[\text{OH}]$ and J_3 are taken from the model mechanism. A 1 min averaging time was used for R and found to give satisfactory results.

Table 3 shows the contribution of various isoprene routes to formaldehyde production. The table also shows the total percentage contribution of isoprene to the overall rate of forming HCHO. The latter was calculated from the model mechanism. Some of the HCHO production rates peak around solar noon (e.g. ISOPBO and ISOPDO) whereas some of the species become more important later on (e.g. HMVKAO, MVK). In terms of total HCHO production from all routes in the isoprene mechanism, there is an increase until 13:00 h followed by a slower decline.

Fig. 4 shows the production of HO₂ from isoprene chemistry from all routes except HCHO, and separately, the HCHO contribution ((R2), (R3a)). This figure demonstrates the major source of the asymmetry in the ob-

served and modelled peroxy radicals on this day. HCHO is acting as a temporary reservoir, slowly releasing the HO₂ radicals throughout the afternoon.

7. NO to NO₂ conversions

There are 85 peroxy radicals in the model, that can each react with NO to produce NO₂. The NO₂ then forms O₃ through reactions (R8) and (R9). Table 4 shows the fraction of NO to NO₂ conversions due to the complete oxidation of each of the hydrocarbons and CO in the model. The table also shows the total conversion rate of NO to NO₂ by all 85 peroxy radicals in the model in ppb h⁻¹.

The NO to NO₂ conversions through peroxy radicals are of the order of 2 ppb h⁻¹, and isoprene is responsible for 20–40% of the total. Isoprene is the single most important component in terms of NO to NO₂ conversions, with smaller but significant contributions from CO, CH₄ and the butenes. By contrast, CO is the most important primary species for OH removal, although isoprene is as important around midday (Table 1). It follows, therefore, that isoprene secondary chemistry is responsible for many of its NO to NO₂ conversions.

If it is assumed that the NO₂ formed in this manner goes on to produce O₃, the production rate can be used to calculate O₃ concentrations, and this has been carried out in Fig. 2. The ozone has been calculated by using the observed value at 9:30, and adding on the model produced ozone according to the production rates in Table 4. The good agreement between measurements and O₃ predicted in this manner suggests that most of the O₃ diurnal cycle at Mace Head is due to photochemical production. At times, this method under predicts O₃,

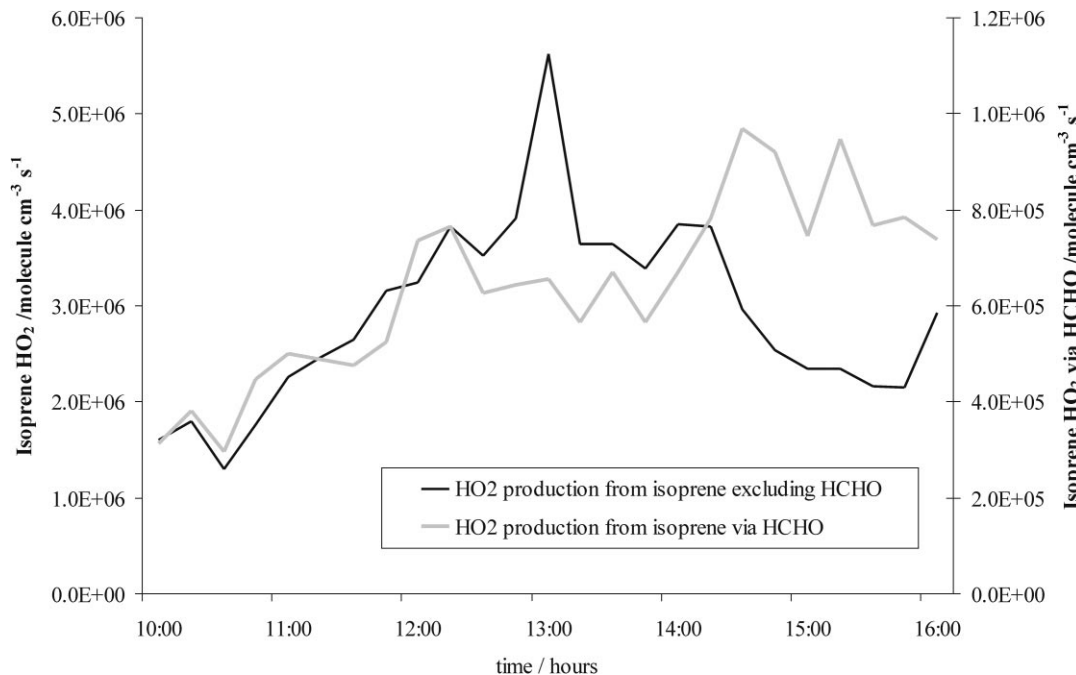


Fig. 4. HO₂ production from isoprene chemistry shown as total production minus the HCHO contribution (black line), and that from HCHO only (grey line).

Table 4

NO to NO₂ conversions by peroxy radicals as a % of the total, and the conversion rate of NO to NO₂ by all peroxy radicals in ppb h⁻¹ on 17 July 1996

Species	10:00	11:00	12:00	12:30	13:00	14:00	15:00	16:00
Carbon monoxide	26.6	21.6	17.0	14.7	15.8	16.8	19.9	22.4
Methane	20.9	16.8	15.1	12.6	12.9	14.1	16.4	17.0
Ethane	0.6	0.6	0.4	0.7	0.5	1.4	0.7	0.5
Ethene	0.1	0.7	0.4	0.4	0.3	0.3	0.5	0.3
Propane	0.8	0.4	0.3	0.3	0.4	0.4	0.3	0.4
Propene	3.1	4.4	4.1	4.2	3.9	3.7	3.3	2.8
<i>Cis</i> - and <i>trans</i> -2-Butene	16.5	17.3	15.0	16.4	15.2	15.1	15.8	17.1
Isoprene	19.5	27.9	37.9	41.2	42.0	38.6	33.4	28.8
1,3-butadiene	0.6	1.0	0.9	0.8	0.8	0.9	1.0	1.0
1,3,5-Trimethylbenzene	2.7	2.5	2.0	2.1	1.9	2.5	1.9	2.6
Toluene	0.5	0.4	0.5	0.4	0.5	0.6	0.6	0.6
ppb h ⁻¹	1.8	1.7	2.0	2.4	2.6	2.2	1.9	1.9

which probably implies that some of the measured O₃ has been formed previously in the high NO_x conditions advected from the source region. It should also be noted that there may exist dynamical inadequacies in the observationally constrained box model used for this exercise, as transport of species in and out of the box is not considered.

The amount of OH that reacts directly with isoprene compared with the amount that reacts with the second-

ary products of isoprene oxidation has been expressed as a ratio in Fig. 5. For the first part of the day, Fig. 5 shows that the amount of OH reacting with isoprene is roughly double that reacting with its oxidation products. However, as the day progresses and especially after about 14:00 h, the secondary products become much more important in terms of reacting with OH. By 16:00 h, the secondary products are reacting with almost 8 times as much OH as the isoprene itself. It is essential, therefore,

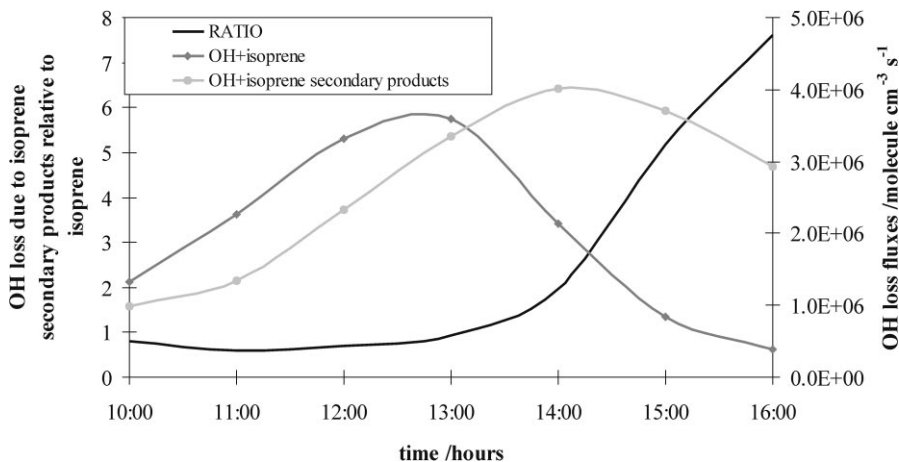


Fig. 5. Ratio of the amount of OH that reacts with isoprene compared with the amount that reacts with secondary products of isoprene chemistry on 17 July 1996.

that the secondary products of isoprene oxidation are also considered explicitly in models, in order to assess the full effect of isoprene chemistry.

8. Conclusions

In this paper, we have attempted to demonstrate the ways in which isoprene chemistry can impact on the local chemistry of a clean air site. We have demonstrated that even relatively small concentrations of isoprene can significantly impact the chemistry of a clean air site.

Looking to the future, Fehsenfeld et al. (1992) report that although increased urbanisation leads to trees being felled, it also causes an enhancement of the urban heat island effect, which more than outweighs the effect of removing trees in terms of isoprene emissions. In addition, because temperature controls isoprene emissions, global warming may lead to greater emissions in the future (Fehsenfeld et al., 1992).

It is clear that because of its climate, Northern Europe is not a large producer of isoprene. However, this study has shown that isoprene can still have an impact in certain locations that are subject to semi-polluted air with a source of isoprene nearby, such as the Mace Head site. Conditions such as these appear to favour O_3 production, and HO_2 production through HCHO. Indeed, the conditions that prevailed on 17 July 1996 at Mace Head have provided a unique opportunity to study in detail the chemistry of isoprene. This study has also demonstrated the strengths of a detailed mechanism such as the MCM, which has allowed us to gain a much deeper insight into atmospheric chemistry than we could have gained with simplified mechanisms.

Acknowledgements

We would like to thank the NERC ACSOE program for funding. NB would like to acknowledge NERC for a studentship. N.C. and M.J.P. acknowledge financial support from NERC (GR3/11958) and the UK Department of the Environment, Transport and the Regions. We would also like to acknowledge the constructive comments of two anonymous referees. This is ACSOE publication number ACP071.

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