

# Aspects of the kinetics and mechanism of the gas-phase reactions of ozone with conjugated dienes

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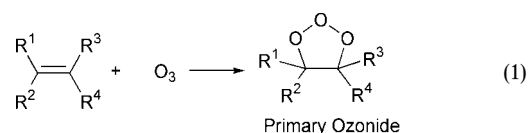
The relative-rate method was used to measure room-temperature rate constants for the gas-phase reactions of ozone with six conjugated dienes under 'OH-free' conditions. Separate experiments were carried out to determine the yields of hydroxyl radical formed from the ozonolyses of four of these compounds, and for buta-1,3-diene and isoprene, using hydroxyl radical scavenger and tracer-type experiments. The following rate constants were obtained at  $298 \pm 5$  K and  $760 \pm 10$  Torr, in units of  $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ :  $43.1 \pm 9.9$  (*E*-penta-1,3-diene),  $27.8 \pm 3.7$  (*Z*-penta-1,3-diene),  $26.2 \pm 6.9$  (2,3-dimethyl-buta-1,3-diene),  $23.9 \pm 5.5$  (5-methylhexa-1,3-diene, mixture of *E*- and *Z*-isomers),  $25.3 \pm 2.3$  (5,5-dimethylhexa-1,3-diene, mixture of *E*- and *Z*-isomers) and  $3060 \pm 880$  (5-dimethylhexa-2,4-diene). The hydroxyl radical formation yields determined, relative to alkene consumed, were:  $0.06 \pm 0.03$  (buta-1,3-diene),  $0.53 \pm 0.16$  (isoprene),  $0.82 \pm 0.25$  (*Z*-penta-1,3-diene),  $0.83 \pm 0.25$  (*E*-penta-1,3-diene),  $0.66 \pm 0.25$  (5-methylhexa-1,3-diene, mixture of *E*- and *Z*-isomers) and  $0.95 \pm 0.25$  (2,3-dimethylbuta-1,3-diene). The rate parameters are analysed in terms of frontier orbital theory, and the mechanism of OH formation in the ozonolysis of conjugated dienes is discussed.

## Introduction

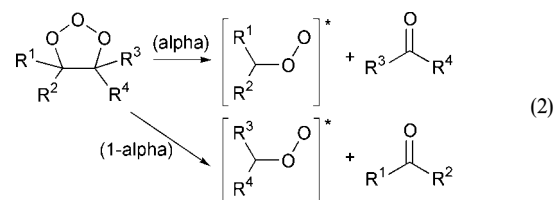
Study of the gas-phase reactions of ozone with alkenes is an active area of research for a number of reasons. In the atmosphere, the reactions contribute directly to the oxidation of unsaturated VOCs,<sup>1,2</sup> they inject significant amounts of carbonyl<sup>3</sup> and organic acid<sup>4</sup> products into the troposphere, they contribute to the formation of organic aerosols,<sup>5</sup> and they lead to the direct production of HO<sub>x</sub> species including the hydroxyl radical, OH.<sup>6–9</sup> However, despite the wealth of experimental and theoretical data available, the mechanism for the gas-phase ozonolysis of monoalkenes is still not fully understood. The ozonolysis reactions of conjugated dienes have been only scantily examined, and little is known about the mechanism of the reactions, although conjugated dienes are important trace components of the atmosphere. Of the biogenic VOCs, isoprene (2-methylbuta-1,3-diene) is emitted at the greatest rate; in the UK, it is primarily released from the Sitka spruce tree which constitutes 25% of the coverage of all woodlands, an area totalling around 530 kha.<sup>10</sup> On the global scale, total emissions of biogenic VOCs are estimated to be *ca.* 1150 Tg yr<sup>-1</sup> of which 530 Tg yr<sup>-1</sup> is isoprene.<sup>11</sup> Additionally, the monoterpenes  $\alpha$ -phellandrene,  $\beta$ -phellandrene and  $\alpha$ -terpinene are all conjugated diene species. In terms of anthropogenic emissions, isoprene and buta-1,3-diene are significant constituents of car exhaust emissions,<sup>12</sup> which also contain a number of other conjugated diene species including 1-methylcyclopenta-1,3-diene and cyclohexa-1,3-diene.<sup>13</sup> Classified as a hazardous air pollutant, buta-1,3-diene is included in many emission measurement inventories, and its atmospheric reactions have been the subject of renewed experimental investigation.<sup>14,15</sup>

Any elucidation of the reaction mechanism of the reactions between ozone and conjugated dienes is thus of value in its own right, and may also help shed light on some of the areas of uncertainty in terms of the broader ozone–alkene reaction

mechanism as a whole. It is generally accepted that the ozonolysis mechanism is an electrocyclic process (specifically a [3 + 2] cycloaddition) whereby the reacting valence electrons are redistributed through a cyclic transition state that gives rise to the first intermediate reaction product, the primary ozonide (POZ).<sup>16</sup>



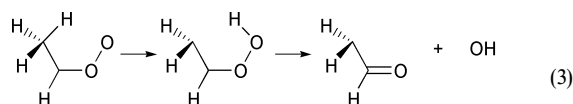
Due to the exothermicity of reaction (1), the POZ is formed in a vibrationally excited state and rapidly decomposes to give a pair of Criegee intermediates (CI) and carbonyl compounds for asymmetric alkenes, or one of each for symmetric alkenes.



The CIs formed are usually assumed to be vibrationally excited† and may either be collisionally stabilised or decompose, and it is the result of this latter reaction that is generally believed to be responsible for the formation of OH radicals. It has been suggested, and there is a growing body of evidence to support this,<sup>1</sup> that the OH forming decomposition pathway of the excited CI (in some cases the major pathway) involves a

† However, very recent work<sup>8</sup> seems to indicate that decomposition at one atmosphere is a thermal process.

1,4-sigmatropic hydrogen atom shift, that yields a hydroperoxide intermediate which subsequently releases OH.<sup>17</sup>



A number of kinetic determinations have been made for the reactions of ozone with various conjugated diene species, but the data set is limited. A correlation has been presented by King *et al.*<sup>18</sup> for the reactions of ozone with a large group of monoalkenes and a smaller number of conjugated dienes. The two groups of compounds show different linear relationships between the negative logarithm of room temperature rate constants and calculated alkene HOMO energies ( $E_{\text{HOMO}}$ ). OH yields have been reported for the reactions of ozone with buta-1,3-diene,<sup>15,19</sup> 2-methylbutadiene (isoprene),<sup>6,20–25</sup> and  $\beta$ -phellandrene.<sup>20</sup> As indicated in Table 1, there is some disparity in the OH yield determinations reported for isoprene, with Atkinson *et al.* quoting 0.27,<sup>20</sup> Paulson *et al.* 0.25,<sup>22</sup> Neeb and Moortgat 0.26,<sup>23</sup> Gutbrod *et al.* 0.19<sup>21</sup> and Rickard *et al.* 0.44.<sup>24</sup> The table also contains two additional values for isoprene but it should be noted that the value of 0.68 obtained by Paulson *et al.*<sup>25</sup> was determined from a tracer experiment, where the yield of OH was determined by the diminution in the concentration of added methylcyclohexane. Due to the relatively small amounts of the scavenger destroyed (a consequence of the rate constant for the reaction of OH with methylcyclohexane) the uncertainty ascribed to this result is very high. The OH yield from the reaction of ozone with isoprene reported by Donahue *et al.*, of *ca.* 0.50,<sup>6</sup> must also be taken with some caution as although OH was measured directly by LIF, the experiment was carried out at only a few Torr total pressure. The value obtained by Rickard *et al.* thus appears anomalous in the light of the remaining determinations.

**Table 1** Summary of literature OH yields for conjugated dienes

Diene		OH yield	Ref.
1,3-Butadiene		$0.08^{+0.04}_{-0.03}$	19
1,3-Butadiene		$0.13 \pm 0.03$	15
Isoprene		$0.27^{+0.13}_{-0.09}$	20
Isoprene		$0.68 \pm 0.15$	25
Isoprene		$0.19 \pm 0.02$	21
Isoprene		$0.50 \pm 0.03$	6
Isoprene		$0.25 \pm 0.06$	22
Isoprene		$0.44 \pm 0.11$	24
Isoprene		$0.26^{+0.03}_{-0.06}$	23
$\beta$ -Phellandrene		$0.14^{+0.07}_{-0.05}$	25

The aim of the experiments carried out in the present study was to extend the available datasets for the kinetics and OH yields of the reactions of ozone with conjugated butadienes.

## Calculations

The energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) of each alkene studied was calculated using MOPAC6<sup>26</sup> at a semi-empirical level. All molecular geometries were optimised to the default criteria within the package. Orbital energies were obtained from the eigenvalue solutions of the molecular wavefunctions using a PM3 Hamiltonian.<sup>27,28</sup> The highest occupied molecular orbital energy,  $E_{\text{HOMO}}$ , is related directly to the ionisation potential according to Koopmans' theorem, being equal in magnitude, but opposite in sign. In addition, the contributions of the carbon  $p_x$ ,  $p_y$  and  $p_z$  orbitals to the HOMO were analysed to give a combined orbital coefficient in the direction perpendicular to the plane of the alkene double bond, for each  $\pi$ -bonded atom in the diene moiety.

## Experimental

The experimental apparatus employed for this study comprised a static reaction chamber with attached GC-FID detection. Experiments were carried out at  $298 \pm 2$  K. A mixture of the alkene under study and a hydroxyl radical scavenger (sufficient cyclohexane or butan-2-ol to scavenge  $\geq 95\%$  of any OH radicals formed for the kinetic and scavenger-type OH yield experiments respectively; between 50 and 100 ppmv *meta*-xylene or 10–20 ppmv (parts per million per volume) 1,3,5-trimethylbenzene for tracer-type OH yield experiments) was prepared in a 50 L collapsible Teflon chamber using dry synthetic air (BOC) as the diluent gas. A typical initial concentration of the alkene was 10–20 ppmv. Experiments were carried out by admitting a known concentration of ozone, at a pressure of *ca.* 8 Torr, into a 0.5 L borosilicate glass reaction vessel and adding a sample of the hydrocarbon mixture such that a total pressure of one atmosphere ( $760 \pm 10$  Torr) was effected. Ozone was generated as a mixture in  $\text{O}_2$  by passing oxygen through a Fischer ozone generator, and its purity was determined spectrophotometrically by absorption at  $\lambda = 254$  nm. After sufficient time for complete reaction, the contents of the glass bulb were separated and detected by gas chromatography (Perkin-Elmer, model 8420 employing a 25 m, 0.53 mm diameter, Poraplot Q capillary column) with flame ionisation detection. This procedure was typically repeated for six different initial ozone concentrations during each study. A typical temperature program employed for the kinetic and tracer-type OH yield experiments held the column isothermally at  $150^\circ\text{C}$  and a carrier gas pressure of 20 psi was employed. For scavenger-type OH yield experiments, the column was held at  $100^\circ\text{C}$  for 1.5 min before being raised to  $200^\circ\text{C}$  at a rate of  $15^\circ\text{C min}^{-1}$ . The column was then held at this temperature for a further 4.5 min, a carrier gas pressure of 10 psi being used throughout. All gaseous reagents used were  $\geq 95\%$  in purity and were used without further processing; all other reagents employed were of analytical grade and underwent a freeze–pump–thaw cycle before being used. For the various OH yield experiments, and for reaction stoichiometry experiments chromatographic peak heights were converted into concentrations after calibration with pure standards. The experimental apparatus has been used previously in the measurement of ozone–alkene reaction rate constants<sup>29</sup> and was characterised by measuring relative-rate constants for the reactions of ozone with a number of different pairs of alkenes for which room-temperature reaction rate constants are known. In all cases the relative-rate constants obtained were within *ca.* 10% of values determined on the basis of literature rate constants.

## Results

### Kinetic experiments

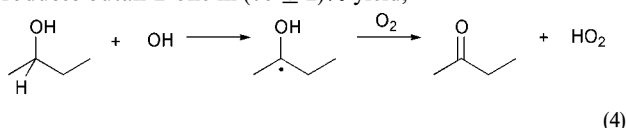
Experimental results obtained in the presence of cyclohexane were analysed using the standard relative-rate expression,<sup>25</sup>

$$\ln([A]_i/[A]) = (k_A/k_B)\ln([B]_i/[B]) \quad (I)$$

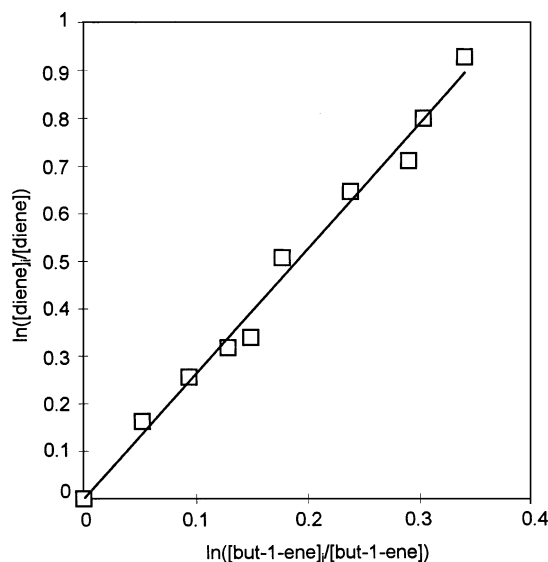
( $k_A$  and  $k_B$  are the rate constants for reaction of dienes A and B with ozone, [A] and [B] are their concentrations after reaction, and  $[A]_i$  and  $[B]_i$  are their initial concentrations). A plot of  $\ln([A]_i/[A])$  vs.  $\ln([B]_i/[B])$  yielded the relative rate constants listed in Table 2 for each compound studied during this investigation. An example relative-rate plot is included in Fig. 1 for 5,5-dimethylhexa-1,3-diene (mixture of the *E*- and *Z*-isomers, with but-1-ene being used as the reference compound).

### OH yields

**Scavenger experiments.** The reaction of OH with butan-2-ol produces butan-2-one in  $(60 \pm 2)\%$  yield,<sup>30</sup>



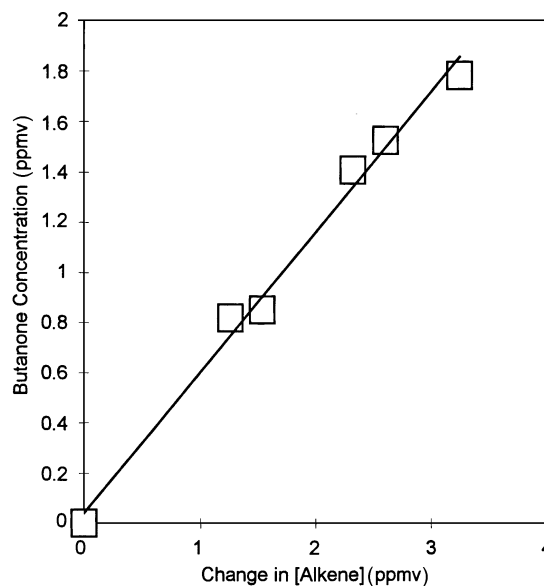
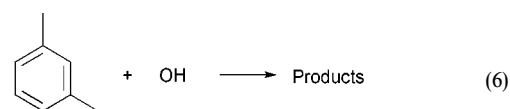
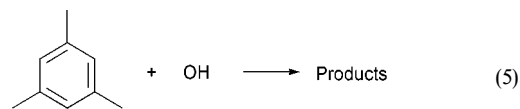
and this reaction has been used by Chew and Atkinson<sup>31</sup> to determine OH yields for a number of ozonolysis reactions. In the present study, this type of scavenger experiment was carried in the presence of sufficient butan-2-ol such that reaction (4) accounted for  $\geq 95\%$  of the fate of any OH formed. A



**Fig. 1** Relative-rate plot for 5,5-dimethylhexa-1,3-diene (mixture of *E*- and *Z*-isomers), with but-1-ene as the reference compound. ( $y = (2.62 \pm 0.10)x + (0.0014 \pm 0.021)$ , standard errors.)

typical plot of the experimental data, i.e.  $[\text{butanone}]_{\text{formed}}$  vs.  $\Delta[\text{alkene}]$ , is shown in Fig. 2 for *Z*-penta-1,3-diene. OH formation yields, with respect to alkene consumed, are simply obtained by dividing the slope of such plots by 0.60.

**Tracer experiments.** These experiments, which have been described previously,<sup>24</sup> involve the ozonolysis of a chosen diene in the presence of a hydroxyl radical tracer compound. The tracers employed were 1,3,5-trimethylbenzene and *meta*-xylene, both of which react relatively quickly with OH ( $k_5 = 5.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_6 = 2.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>32,33</sup> but do not react with ozone under the conditions of the experiments where the concentration of diene is always in excess of that of ozone.



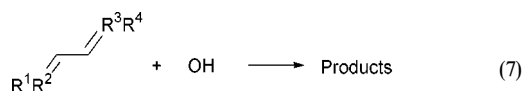
**Fig. 2** Plot of  $[\text{butanone}]$  vs.  $\Delta[\text{alkene}]$  used to obtain the OH yield for *Z*-penta-1,3-diene. ( $y = (0.56 \pm 0.03)x + (0.04 \pm 0.06)$ , standard errors.)

**Table 2** Summary of measured rate data

Diene	Reference compound	Relative rate <sup>a</sup>	$k_{\text{ozone}}/10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>a</sup>
<i>E</i> -Penta-1,3-diene	Isoprene <sup>b</sup>	$3.41 \pm 0.78$	$43.1 \pm 9.9$
<i>Z</i> -Penta-1,3-diene	Isoprene <sup>b</sup>	$2.21 \pm 0.29$	$27.8 \pm 3.7$
2,3-Dimethylbuta-1,3-diene	Isoprene <sup>b</sup>	$2.05 \pm 0.54$	$26.2 \pm 6.9$
5-Methylhexa-1,3-diene (mixture of <i>E</i> - and <i>Z</i> -isomers)	Isoprene <sup>b</sup>	$1.87 \pm 0.43$	$23.9 \pm 5.5$
5,5-Dimethylhexa-1,3-diene (mixture of <i>E</i> - and <i>Z</i> -isomers)	But-1-ene <sup>c</sup>	$2.62 \pm 0.23$	$25.3 \pm 2.3$
2,5-Dimethylhexa-2,4-diene	2,3-Dimethylbut-2-ene <sup>d</sup>	$2.70 \pm 0.78$	$3060 \pm 880$

<sup>a</sup> Errors are statistical at the 95% confidence level. <sup>b</sup> Reference rate constant used was  $k = (1.28 \pm 0.32) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

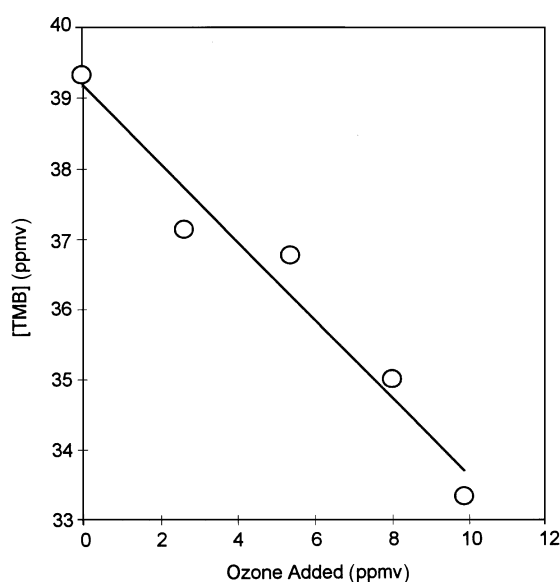
<sup>c</sup> Reference rate constant used was  $k = (9.64 \pm 2.41) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>d</sup> Reference rate constant used was  $k = (1.13 \pm 0.39) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .



The OH formation yield is calculated by determining the fraction of OH that will react with the tracer (the quotient in eqn. (8)), and thus for experiments using 1,3,5-trimethylbenzene (TMB) as scavenger:

$$[\text{TMB}] = [\text{TMB}]_0 - \frac{k_5[\text{TMB}]}{k_5[\text{TMB}] + k_7[\text{diene}] + k_{\text{loss}}} \beta \Delta[\text{O}_3] \quad (8)$$

Here,  $[\text{TMB}]_0$  is the initial concentration of TMB,  $\beta$  is the yield of OH formation with respect to ozone consumed and  $k_{\text{loss}}$  represents other loss processes for OH, including reaction with products. For small  $\Delta[\text{O}_3]$ , a plot of  $[\text{TMB}]$  vs.  $\Delta[\text{O}_3]$  is linear with a slope of  $-k_5[\text{TMB}]_i\beta/(k_5[\text{TMB}]_i$



**Fig. 3** Plot of  $[\text{TMB}]$  vs.  $[\text{O}_3]_{\text{added}}$  for the measurement of the OH yield of Z-penta-1,3-diene by the scavenger method. ( $y = (-0.56 \pm 0.07)x + (39.2 \pm 0.4)$ , standard errors.)

**Table 3** Summary of measured OH yields

Diene	$\Delta[\text{diene}]/\Delta[\text{O}_3]$	OH yield <sup>a</sup>			
		butan-2-ol	TMB	<i>m</i> -XYL	Preferred <sup>b</sup>
	$1.00 \pm 0.19$	(0.17) <sup>c</sup>	—	0.06	$0.06 \pm 0.03$
	$1.08 \pm 0.20$	0.59	0.45	0.55	$0.53 \pm 0.16$
	$1.16 \pm 0.18$	0.93	0.71	—	$0.82 \pm 0.25$
	$1.14 \pm 0.08$	0.90	—	0.75	$0.83 \pm 0.25$
	$1.11 \pm 0.24$	—	0.68	0.64	$0.66 \pm 0.20$
	$1.22 \pm 0.11$	—	0.80	1.11	$0.95 \pm 0.29$

<sup>a</sup> Relative to alkene consumed. <sup>b</sup> Mean value except for butadiene (see text), errors represent estimated total (statistical and systematic) uncertainty. <sup>c</sup> Not used for preferred OH yield.

+  $k_6[\text{diene}] + k_{\text{loss}}$ ), and  $k_{\text{loss}} \approx 0$ . Thus a plot of  $[\text{TMB}]/\Delta[\text{O}_3]$  vs.  $k_5[\text{TMB}]_i\beta/(k_5[\text{TMB}]_i + k_7[\text{diene}])$  yields a straight line with slope  $\beta$ . The same treatment is applied to experiments using *meta*-xylene as OH-tracer but using  $k_6$  in place of  $k_5$ . A plot of the tracer raw data for the ozonolysis experiment of Z-penta-1,3-diene in the presence of TMB is included in Fig. 3.

All OH yields determined by the two methods are listed in Table 3 (two determinations were made for each compound) along with reaction stoichiometries. These latter values were measured using exactly the same experimental procedure as for a relative-rate experiment, but with only one diene present.

## Discussion

### Kinetics

Of the measured rate constants listed in Table 2, only three have been previously reported. The values obtained in this investigation (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for Z-penta-1,3-diene, *E*-penta-1,3-diene and 2,3-dimethylbuta-1,3-diene of  $27.8 \pm 3.7 \times 10^{-18}$ ,  $43.1 \pm 9.9 \times 10^{-18}$  and  $26.2 \pm 6.9 \times 10^{-18}$ , respectively, compare with values determined by Sidebottom and co-workers<sup>34</sup> (who observed the time-resolved decay in the concentration of ozone) of  $28.5 \pm 2.9 \times 10^{-18}$ ,  $47.4 \pm 5.4 \times 10^{-18}$  and  $24.9 \pm 1.9 \times 10^{-18}$ . The agreement is very good, and certainly within the mutual uncertainties of each of the determinations. The Arrhenius parameters for the reaction of ozone with 2,3-dimethylbuta-1,3-diene have also previously been determined by Treacy *et al.*,<sup>35</sup>—again using an absolute method—and a room temperature rate constant of  $25.7 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained, again in excellent agreement with the current investigation.

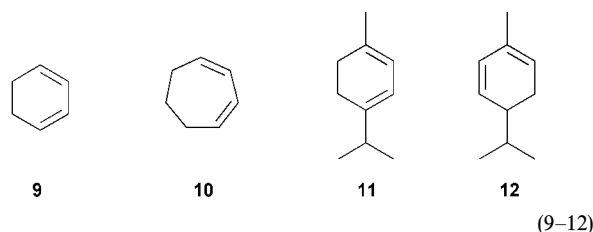
As mentioned in the introductory section, there is a linear relationship between the logarithm of the room temperature rate constant for the reactions of ozone with alkenes, and the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) of the alkene. This relationship has been highlighted in a number of previous studies and is rationalised in terms of frontier molecular orbital theory.<sup>36</sup> Formation of the primary ozonide occurs *via* a pericyclic reaction in which the reacting valence electrons are rearranged through a cyclic transition state and electron density is transferred from the HOMO of the alkene to the lowest unoccupied molecular orbital (LUMO) of ozone. Thus, in a large part, the HOMO–LUMO gap determines the activation barrier for the reaction. As  $E_{\text{LUMO}}$  is the same in



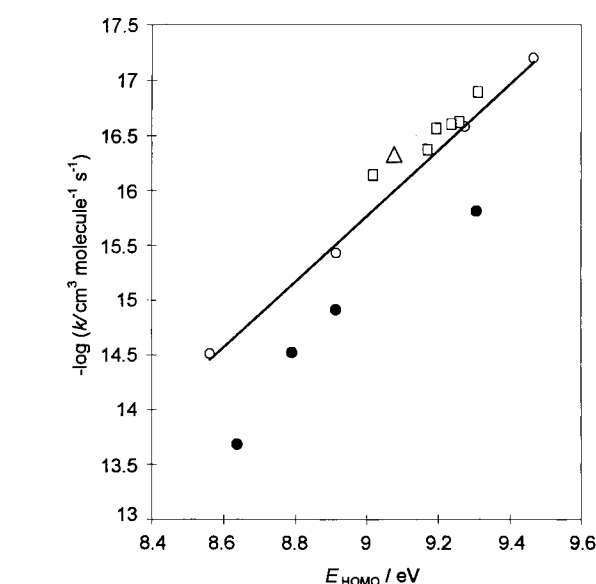
each case, and as the activation barrier appears in the exponent of the Arrhenius expression, the logarithm of the rate constant is linearly related to the value of  $E_{\text{HOMO}}$  for each alkene. A further consequence of the concerted nature of the ozonolysis mechanism is that any asymmetry in the size of the HOMO lobes at each end of the double bond, will have the effect of retarding the ease with which HOMO and LUMO can interact thus reducing the reaction rate. Orbital asymmetry effects have been investigated previously in this laboratory for a range of asymmetric monoalkenes. However, orbital coefficient effects have not been investigated for the reactions of ozone with conjugated dienes, to date.

Table 4 summarises the kinetic data from Table 2 and includes values taken from the literature for ten other conjugated diene species. Also included in the table are calculated values of  $E_{\text{HOMO}}$  for each diene, and orbital coefficient contributions to the HOMO (in the direction perpendicular to each individual double bond) at each of the four  $\pi$ -bonded carbon atoms. A plot of the negative logarithm of the rate constant *vs.*  $E_{\text{HOMO}}$  comprises Fig. 4. The indicated regression line is constructed with respect to the wholly symmetric dienes; buta-

1,3-diene, 2,3-dimethylbuta-1,3-diene, *E,E*-hexa-2,4-diene and 2,5-dimethylhexa-2,4-diene. As can be seen from the figure, the correlation between  $-\log k$  and  $E_{\text{HOMO}}$  is strong, but with four striking outliers; cyclohexa-1,3-diene, cyclohepta-1,3-diene,  $\alpha$ -terpinene and  $\alpha$ -phellandrene (structures 9–12 respectively).



What these compounds have in common is a fixed conformation in which the double bonds are held *cisoid* to one another. A line drawn through the four data points corresponding to these compounds is almost exactly parallel to the regression line indicated in that figure, but is displaced downwards by a value of about 1.0 which is to say that these compounds react about one order of magnitude faster with ozone than would be expected from the simplest application of frontier molecular orbital theory to the ozonolysis mechanism. It is possible that the larger observed rate constants for the reactions of ozone with the cyclic *cisoid*-dienes are due to the effects of ring strain lowering the energy of the transition state for rupture of the primary ozonide. The four carbon atoms of a diene  $\pi$ -system are expected to be energetically most stable when coplanar, but the 6-membered ring will not fully permit this. However, if ring strain were the cause of the anomalously large rate constants, it might be expected that the rate constant for the reaction of ozone with  $\beta$ -phellandrene might be intermediate between the values expected for the two groups. At first sight, this compound behaves like the open-chain compounds, which are expected to have *transoid* structures. (As we shall see later,  $\beta$ -phellandrene actually reacts more slowly than expected on the basis of the open-chain compounds.) It is not clear why the cyclic *cisoid* dienes react more quickly than the *transoid* compounds.



**Fig. 4** Plot of  $-\log k$  *vs.*  $E_{\text{HOMO}}$  for the reactions of  $\text{O}_3$  with dienes. Open symbols, *transoid* dienes; filled symbols, *cisoid* dienes; open circles, symmetrical dienes; open triangle,  $\beta$ -phellandrene. (Best-fit line,  $y = (2.97 \pm 0.12)x - (10.0 \pm 1.1)$ , standard errors.)

**Table 4** Summary of calculated molecular properties and negative logarithm values of room-temperature rate constants

Diene	$E_{\text{HOMO}}/\text{eV}$	$-\log k^a$	$c_1^{b,c}$	$c_2$	$c_3$	$c_4$
1,3-Butadiene	9.47	17.20 <sup>d</sup>	0.562	0.430	0.430	0.562
2,3-Dimethylbuta-1,3-diene	9.28	16.58	0.537	0.397	0.397	0.537
<i>E,E</i> -hexa-2,4-diene	8.92	15.43 <sup>d</sup>	0.521	0.421	0.421	0.521
2,5-Dimethylhexa-2,4-diene	8.56	14.51	0.501	0.420	0.420	0.501
Isoprene	9.34	16.89 <sup>d</sup>	0.505	0.368	0.455	0.599
<i>E</i> -penta-1,3-diene	9.17	16.47	0.521	0.369	0.465	0.540
<i>Z</i> -penta-1,3-diene	9.20	16.56	0.521	0.372	0.474	0.549
2,4-Dimethylpenta-1,3-diene	9.02	16.14 <sup>e</sup>	0.520	0.353	0.478	0.511
5-Methylhexa-1,3-diene	9.28	16.62	0.505	0.376	0.468	0.555
(average values for <i>E</i> / <i>Z</i> -isomers)						
5,5-Dimethylhexa-1,3-diene	9.25	16.60	0.534	0.388	0.463	0.557
(average values for <i>E</i> / <i>Z</i> -isomers)						
<i>E</i> -2-Methylpenta-1,3-diene	9.11	16.10 <sup>e</sup>	0.566	0.400	0.427	0.514
$\beta$ -Phellandrene	9.08	16.33 <sup>d</sup>	0.562	0.399	0.426	0.516
Cyclohexa-1,3-diene	8.91	14.91 <sup>d</sup>	—	—	—	—
Cyclohepta-1,3-diene	9.31	15.81 <sup>d</sup>	—	—	—	—
$\alpha$ -Terpinene	8.64	13.68 <sup>d</sup>	—	—	—	—
$\alpha$ -Phellandrene	8.79	14.52 <sup>d</sup>	—	—	—	—

<sup>a</sup>  $k$  in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>b</sup> Suffix refers to carbon atom within the  $\pi$ -system. Carbon atom 1 is designated as the first carbon atom of the least substituted of the double bonds. <sup>c</sup> Wavesigns not indicated. <sup>d</sup> Ref. 37. <sup>e</sup> Ref. 34.

**Table 5** Summary of data indicating deviation in logarithm of rate constant from linear relationship indicated in Fig. 4

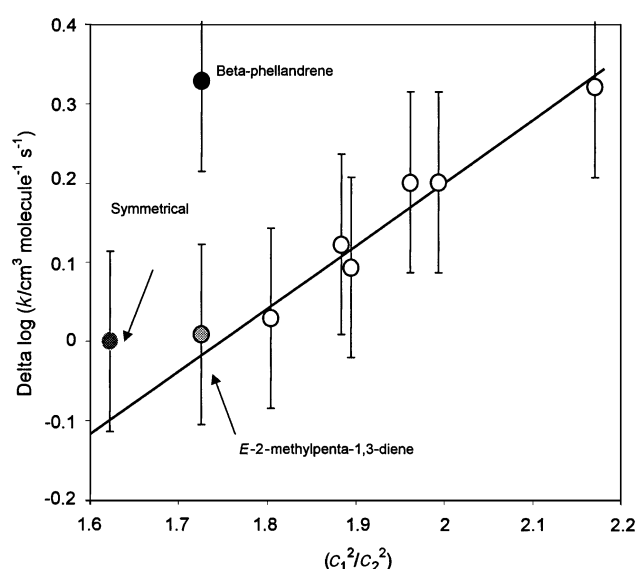
Diene	$-\log k^a$ (measured)	$-\log k^a$ (predicted)	$-\Delta \log k^b$	$c_1^2/c_2^2$
<i>E</i> -Penta-1,3-diene	16.47	16.27	0.20	1.99
<i>Z</i> -Penta-1,3-diene	16.56	16.36	0.20	1.96
5-Methylhexa-1,3-diene (mixture of <i>E</i> - and <i>Z</i> -isomers)	16.62	16.59	0.03	1.80
5,5-Dimethylhexa-1,3-diene (mixture of <i>E</i> - and <i>Z</i> -isomers)	16.60	16.50	0.10	1.89
Isoprene	16.89	16.77	0.12	1.88
2,4-Dimethylpenta-1,3-diene	16.14	15.82	0.32	2.17
<i>E</i> -2-Methylpenta-1,3-diene	16.10	16.09	0.01	1.73 <sup>c</sup>
$\beta$ -Phellandrene	16.33	16.00	0.33	1.73 <sup>c</sup>

<sup>a</sup>  $k$  in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>b</sup>  $\Delta \log k = (-\log k_{\text{measured}}) - (-\log k_{\text{predicted}})$ . <sup>c</sup> Ratios are averaged over the two double bonds; see text.

Closer scrutiny of Fig. 4 reveals that the data points (fixed *cisoid* dienes apart) for asymmetric dienes lie above the indicated regression line, which is constructed with respect to the four symmetric dienes. Analysis of the magnitude of deviation of each data point in Fig. 4, away from the indicated regression line (*i.e.*  $\Delta \log k$ ) with respect to asymmetry in orbital coefficients at carbon atoms 1 and 2 (the least substituted double bond) and carbon atoms 3 and 4 (the most substituted double bond) may provide some additional information about the reaction mechanism. In a previous study undertaken in this laboratory,<sup>29</sup>  $\Delta \log k$  values were shown to be correlated with the ratio of the squares of orbital coefficients at either end of the double bond in the reactions of ozone with asymmetric monoalkenes. In the case of the ozonolysis of conjugated dienes, ozone has a choice of two double bonds to attack. For the asymmetric conjugated dienes,  $\Delta \log k$  was plotted as a function of  $(c_m/c_n)^2$  for all possible combinations of  $m$  and  $n$  between 1 and 4. (The bond joining carbon atom 1 to carbon atom 2 is the least substituted.) For  $\beta$ -phellandrene and 2-methylpenta-1,3-diene, both double bonds have the same number of substituents, and these compounds were not included in the plots. The best correlation by far is observed for  $m = 1$ ,  $n = 2$  ( $r^2 = 0.96$ ), this plot is shown in Fig. 5 and the data are summarised in Table 5: Indicated on the plot are error bars representing a 30% error in the measured rate con-







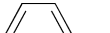


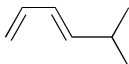


stant. The correlation is very strong, although that may be at least partly fortuitous, given that the scatter in the points is significantly less than might be expected from the uncertainty in the rate constants. For  $\beta$ -phellandrene and *E*-2-methylpenta-1,3-diene, the equal number of substituents at the two double bonds would indicate that  $\Delta \log k$  should be small; this is the case for the pentadiene, but not for  $\beta$ -phellandrene. It may well be that the cyclic nature of the terpene is influencing the reactivity. The data for both of these compounds are included in Fig. 5, but the ratio of coefficients used is the average of the ratios for the two double bonds; *i.e.*  $\{(c_1/c_2)^2 + (c_4/c_3)^2\}/2$ . The average value obtained from the symmetrical dienes used to estimate expected rate constants is also indicated on Fig. 5. One possible explanation for the correlation in the figure is that ozone attacks preferentially at the least substituted double bond, a counterintuitive notion given that increased alkyl-substitution increases the reactivity of monoalkenes. However, a number of studies have shown that the ozonolysis of isoprene gives methacrolein and methylvinylketone in the ratio of approximately two to one, indicating a preference for attack at the least substituted double bond. In order to clarify if this observation is more general, we have measured some carbonyl yields for the ozonolysis of *Z*-penta-1,3-diene, *E*-penta-1,3-diene and 5-methylhexa-1,3-diene. The results are listed in Table 6, and indicate a marked preference for attack at the least substituted double bond; this observation is consistent with the results displayed in Fig. 5.

An interesting feature of the correlation in Fig. 4 is that the slope of the regression line is  $3.0 \pm 0.1$  compared to a value of  $1.9 \pm 0.2$  for a similar plot for simple symmetric monoalkenes. There has been little discussion of the slopes of  $\log k$ - $E_{\text{HOMO}}$  plots in the literature. For the reactions of OH and NO<sub>3</sub> with alkenes, no difference in the slopes for monoalkenes and conjugated dienes is observed. However, it should be noted that



**Fig. 5** Plot of  $\Delta \log k$  vs.  $(c_1/c_2)^2$ . Note that for  $\beta$ -phellandrene and 2-methylpenta-1,3-diene, the ratio of coefficients is the average ratio for the two double bonds; see text.

**Table 6** Measured primary carbonyl yield data. Isoprene data (first row of table) taken from ref. 24

Diene structure	[Carbonyl] <sub>formed</sub> /Δ[alkene]			
		0.13		0.32
		0.09		0.06
		0.13		0.08
		0.07		0.05

although the symmetrical dienes have equivalent double bonds, the electron density distribution across each double bond is not even. In order to compare the diene and monoalkene plots directly, correction to the diene rate constants should be made for the uneven electron density across the double bond. These corrections can be made using the best-fit line from Fig. 4 in ref. 30 to yield a  $\log k_{\text{corr}} - E_{\text{HOMO}}$  plot for the dienes with a slope of  $2.0 \pm 0.4$ , in good agreement with the slope obtained for the monoalkenes. Such corrections are not required for the reactions of OH and  $\text{NO}_3$  with dienes because the rate constants for the reactions of these compounds are independent of asymmetry across the double bond.

## OH yields

The OH yields listed in Table 3 show that there is reasonable agreement between the methods used. It has been pointed out by Chew and Atkinson<sup>31</sup> that scavenging experiments involving the reaction of butan-2-ol can give rise to high OH yields in the ozonolysis of slowly reacting alkenes because impurities in the butan-2-ol can react with  $\text{O}_3$  to generate butanone. In the present work, this effect is most noticeable for butadiene, which of all the dienes studied reacts most slowly with ozone. Furthermore, because this reaction has the lowest OH yield of the reactions studied, the effect of the extraneous OH is to introduce a very large percentage error in the final yield. We therefore prefer to ignore the value for the OH yield obtained from the butanol/butanone experiments for this compound. For the other compounds, the yields from the butanol/butanone experiments are within the expected error of about 30%, and the values from all of the determinations are averaged to give the preferred value. An experiment was also carried out to investigate the reaction of ozone with butan-2-ol directly. The concentration of the alcohol was the same as for the scavenger-type experiments, and a yield of butanone of around 0.30 was obtained, confirming that impurities can affect the measured yields.

The value obtained for the OH yield for the ozonolysis of butadiene is in good agreement with the previous determinations of Atkinson and Aschmann,<sup>19</sup> who obtained an OH yield of 0.08. Kramp and Paulson,<sup>15</sup> however, reported a value of 0.13, a factor of two greater than ours. The origin of this discrepancy is probably just that the methods used by us and by Kramp and Paulson are least accurate for low OH yields. It is, however, worth noting that the value we obtain in the butanol scavenger experiments is within 30% of the Kramp and Paulson yield.

The OH yield obtained for the reaction of ozone with isoprene needs more discussion. With the exception of the value obtained by Donahue *et al.*,<sup>6</sup> all previous determinations have been carried out at pressures close to ambient. While the value of Donahue *et al.* is closest to ours, recent work<sup>8</sup> has shown that under the timescales of their experiments, OH yields are strongly pressure dependent, and so a direct comparison with our work is not possible. Gutbrod *et al.*<sup>21</sup> carried out experiments at atmospheric pressure, but with up to 40 mol% of CO as the OH scavenger. Their yield of  $0.19 \pm 0.02$  is the lowest value so far measured. This group measured OH yields in the ozonolysis of a series of alkenes, and obtained yields that were typically a factor of two to three lower than those of most other groups. As explained in the Introduction, the very high value of  $0.68 \pm 0.15$  reported by Paulson *et al.*<sup>25</sup> has considerable uncertainty associated with it; these workers used methylcyclohexane as a tracer, but this compound reacts about one order of magnitude more slowly with OH than does isoprene.

The OH yields reported by Atkinson *et al.*,<sup>20</sup> Paulson *et al.*<sup>22</sup> and Neeb and Moortgat<sup>23</sup> are in excellent agreement with each other, all being very close to 0.26. These groups

used scavenger, tracer and kinetic methods respectively. In general, OH yields obtained by these groups are in very good agreement with those obtained in our own laboratory.<sup>24</sup> However, our current value of  $0.53 \pm 0.16$  is high by about a factor of two, although it agrees within error with our previous determination (using TMB as a tracer) of  $0.44 \pm 0.11$ .<sup>24</sup> It is difficult to understand the origin of the discrepancy, given that three different methods have been used by the other groups. Impurities in the isoprene sample could, in principle, increase our measured yield, but the isoprene would have had to contain a very large fraction of impurity that has a very large OH yield in its reaction with  $\text{O}_3$ . Furthermore, two samples of isoprene were used for the experiments, with no difference being observed for the OH yields. It is not possible at this stage to say with certainty what the true OH yield for the ozonolysis of isoprene really is. From the perspective of atmospheric chemistry, it is clearly important to resolve this uncertainty.

For the other reactions in this study, no previous determinations of the OH yields have been made. A number of patterns emerge: (1) increasing the substitution around the double bond leads to increased OH yields (2,3-dimethylbutadiene > isoprene > butadiene); (2) the OH yield is enhanced when the substituent has a large number of H atoms on the  $\alpha$  position (Z- and E-penta-1,3-diene > 5-methylhexa-1,3-diene); (3) terminal methyl groups have a stronger effect than internal methyl groups (Z- and E-penta-1,3-diene > isoprene). In qualitative terms, observations (1) and (2) are consistent with what is known about the formation of OH in the ozonolysis of monoalkenes (observation (3) does not have a direct analogy for monoalkenes). For monoalkenes, the OH is believed to be generated following the decomposition of the Criegee intermediate *via* the hydroperoxide mechanism (reaction (3)); a structure activity relationship based on this mechanism and developed in this laboratory is able to predict OH yields to within about 20%. It has also been noted that the stoichiometries ( $\Delta[\text{alkene}]/\Delta[\text{O}_3]$ , obtained in the presence of OH scavenger) of the reactions of ozone with monoalkenes are correlated with the OH yields. In Fig. 6, the stoichiometry-OH yield data from ref. 24 are plotted, along with the results obtained in the present paper. What the plot shows is a clear correlation between the two quantities, and further shows that the behaviour of the dienes and monoalkenes is indistinguishable. The isoprene point fits well with the rest of the data. Using a value of 0.26 for the OH yield for the ozonolysis of isoprene gives a

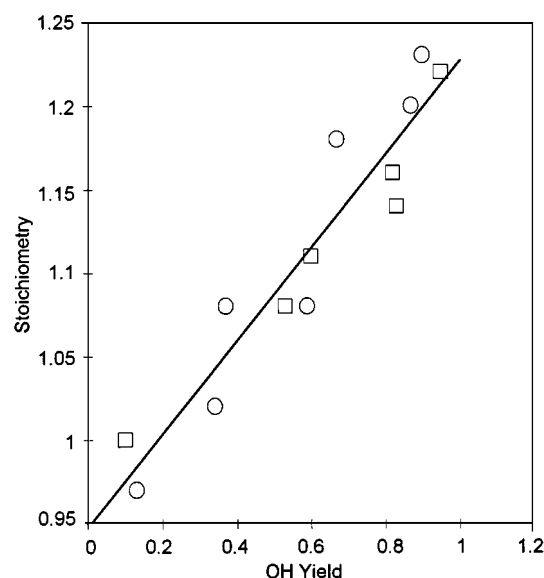
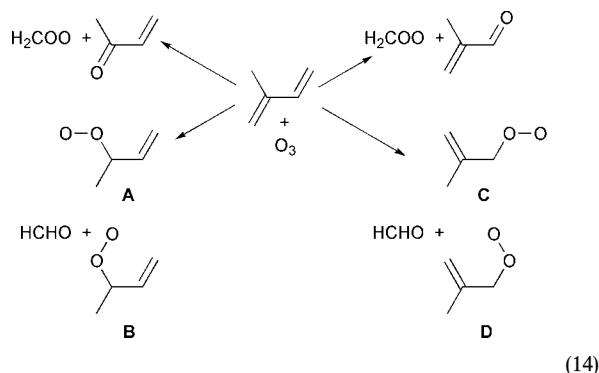


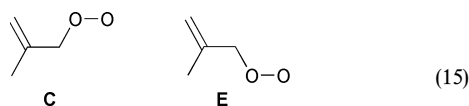
Fig. 6 Plot of stoichiometry vs. OH yield. Open squares, dienes from this work; open circles, monoalkenes from ref. 24.

slightly less good fit, this point lying a little outside the maximum scatter observed for the other compounds. The origin of the correlation between the stoichiometry and the OH yield is not clear. Modelling shows that it cannot be accounted for by the small amount of OH that is not scavenged by the cyclohexane. It may be that the alkene reacts with peroxy radicals generated in the reactions, and this is an area of research that we are currently pursuing.

It is difficult to identify the exact mechanism of OH formation in the reaction of ozone with alkenes. The OH yield increases with substitution, and this indicates a mechanism that is related to the hydroperoxide mechanism for OH formation for monoalkenes. Alternatively, substitution could activate OH formation by some other mechanism. What is clear is that the reactions are complex, giving rise to a range of possible Criegee intermediates.



Given that the *syn*- and *anti*-conformers of methylcarbonyl oxide seem to exist as separate species, it is reasonable to suppose that structures A and B have separate existences. It might even be possible that structures such as C and E exist as separate entities, given the conjugation that runs through the species.



Determining the branching ratios leading to the various species and the efficiency with which each one generates OH radicals is beyond the current ability of experimental chemistry, but it is an area where theoretical methods may have a significant role to play.

## Conclusions

Room-temperature rate constants have been measured for the reactions of ozone with six differently alkyl-substituted dienes in an excess of cyclohexane to scavenge any adventitiously produced OH radicals. The values obtained for *Z*-penta-1,3-diene, *E*-penta-1,3-diene and 2,3-dimethylbuta-1,3-diene are in excellent agreement with previous determinations. The correlation between the  $-\log k$  and  $E_{\text{HOMO}}$  for the reactions of ozone with conjugated dienes has been shown to be different than for the reactions of ozone with monoalkenes, and a clear difference in the reactivity of *cisoid* and *transoid* conjugated dienes has been demonstrated. Analysis of the kinetic data in terms of differences in behaviour between totally symmetric dienes and all other dienes (fixed *cisoid* structures apart) indicates that the reaction rate is retarded by asymmetry in the  $\pi$ -electron density at the least substituted double bond. The measurement of carbonyl yields for some dienes shows a marked preference for addition at this bond.

OH yields have been presented for a systematic range of alkyl-substituted buta-1,3-diene structures. The value obtained for isoprene is around a factor of two higher than measurements made by other groups of workers but is consistent, within error, with a previous determination made in this laboratory. Given the importance of isoprene in the atmosphere, this uncertainty needs to be resolved. The OH yields correlate with reaction stoichiometry in a way that is indistinguishable from the behaviour of monoalkenes. The exact nature of the mechanism for OH formation in the ozonolysis of dienes is not understood, and theoretical studies of this problem would be of great benefit.

## Acknowledgements

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