

PII: S0045-6535(98)00512-8

PRODUCT YIELDS IN THE REACTIONS OF OZONE WITH Z-BUT-2-ENE, E-BUT-2-ENE AND 2-METHYLBUT-2-ENE

C.D. McGill, A.R. Rickard, D. Johnson and G. Marston

Department of Chemistry, University of Reading, Whiteknights, PO Box 224, Reading RG6 6AD, UK

Abstract

Preliminary results on some aspects of the mechanisms of the reactions of ozone with Z-but-2-ene, *E*-but-2-ene and 2-methylbut-2-ene are presented. Primary carbonyl product yields were measured under 'OH-free' conditions and OH yields were determined by monitoring the disappearance of 1,3,5trimethylbenzene. Ethanal yields relative to alkene consumed were measured as 0.86 ± 0.03 , 0.85 ± 0.07 and 0.66 ± 0.02 for the reactions of ozone with Z-but-2-ene, *E*-but-2-ene and 2-methylbut-2-ene, respectively. For 2-methylbut-2-ene, the propanone yield was 0.35 ± 0.03 . Hydroxyl radical yields relative to alkene consumed were measured as 0.33 ± 0.07 , 0.54 ± 0.11 and 0.81 ± 0.16 for the reactions of ozone with *Z*-but-2-ene, *E*-but-2-ene and 2-methylbut-2-ene, respectively.

1. Introduction

The reactions of ozone with alkenes are believed to be important processes in the Earth's atmosphere [1]. As well as being one of the group of reactions that lead to hydrocarbon oxidation, they are also thought to directly generate the hydroxyl radical, OH [2]. Because ozone–alkene reactions occur at night as well as during the day, they can thus lead to OH radicals being present in the atmosphere at night when the usual OH-formation mechanism does not operate [3]. Furthermore, the Criegee intermediates that result from the reactions can oxidise SO_2 to SO_3 [4,5], and also lead to the generation of phytotoxic compounds such as hydroxymethylhydroperoxide [6].

Because of their importance, the kinetics and mechanisms of the gas-phase reactions of ozone with alkenes have been the focus of a huge amount of research. Despite this effort, there are still many unanswered questions about the reactions. In part, problems arose with some of the early work because it was not realised that the reactions generate OH radicals [2]. Consequently, interpretation of experimental observations was often confused by the interfering secondary chemistry initiated by the OH radical. However, although in later work the influence of OH has been accounted for, there have still been difficulties and contradictory results. For example, Grosjean *et al.* [7] published yields for primary carbonyl

products that varied between 0.1 and 1.0 for the reactions of ozone with a series of simple alkenes. However, subsequent work in the same laboratory [8] and by Tuazon *et al.* [9] showed that the total yield of primary carbonyl compounds was usually close to unity. (Interestingly, the original values of Grosjean *et al.* showed an almost exact one-to-one correlation with the OH yields measured by Atkinson and co-workers [10,11].) More recently, the OH yields of Atkinson and co-workers have been brought into question by Gutbrod *et al.* [12] who measured values that were lower by a factor of about two to three. Finally, Schäfer *et al.* concluded on the basis of relative-rate experiments at a pressure of one atmosphere that OH was not the major reactive intermediate formed in the reaction of ozone with alkenes [13]. However, relative-rate experiments by Paulson *et al.* [14] using a wide range of alkenes, but a limited range of reactants indicated that OH was an important intermediate in ozone–alkene reactions, a conclusion supported by a relative-rate study in our laboratory [15] using 2-methylbut-2-ene as the reactive intermediate source, and organic compounds with a wide structural range as reactants. One further piece of evidence has been provided by Donahue *et al.* [16] who have approached the problem from a different perspective and actually measured OH radicals directly in a low-pressure system using laser induced fluorescence.

The question of whether or not OH radicals are formed in ozone-alkene reactions seems now to be settled, although the possibility that some other unidentified intermediate plays some role can not be excluded [14, 16]. In the present paper, we address the discrepancies in product yields, and present preliminary data on primary carbonyl yields and OH yields for the reactions of ozone with Z-but-2-ene (*cis*-but-2-ene), *E*-but-2-ene (*trans*-but-2-ene) and 2-methylbut-2-ene.

2. Experimental

The experimental apparatus employed for this study comprised a static reactant chamber with attached GC-FID detection. A mixture of the alkene under study and the relevant hydroxyl radical scavenger/tracer (cyclohexane for carbonyl yield experiments, and 1,3,5-trimethylbenzene (TMB) for OH-yield experiments respectively) was prepared in a 50 L collapsible Teflon chamber using dry synthetic air (BOC) as the diluent gas; this mixture was used as the reactant reservoir. Typical initial hydrocarbon concentrations employed were between 10-30 ppmv (volume fraction in ppm) of the alkene, 2000 ppmv of cyclohexane and from 10 to 50 ppmv of TMB. Ozone was generated as a mixture in O₂ by passing oxygen through a Fischer ozone generator, its purity being determined spectrophotometrically by absorption at λ =254 nm. Experiments were carried out by admitting a known concentration of ozone (in O₂ at a total 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±10 Torr) was effected. After 10 minutes reaction time 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 (from between 1-30 ppmv) during each study. Chromatographic peak heights were quantified in terms of concentrations after suitable calibration procedures. A typical temperature program employed for carbonyl yield experiments held the column isothermally at 150 °C, whereas OH-yield experiments started with the column at 150 °C, and raising the temperature to 200 °C at a rate of 29.0 °C min⁻¹ at which temperature the column was held for 13 minutes. All gaseous reagents employed 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. Experiments were carried out at 298 ± 3K.

3. Results

The primary carbonyl and OH radical yields obtained in this work for the reactions of ozone with Z-but-2ene, E-but-2-ene and 2-methyl-2-butene are summarised in table 1 along with values obtained by other workers. The details of how these results were obtained are discussed in sections 3.1 and 3.2.

| Alkene | Ethanal | Propanone | ОН |
|-------------------|--|--|--|
| E-but-2-ene | 1.15±0.10 ^a [8] 1.14±0.14 [9] 0.95 [12] 0.85±0.07 ^c [This work] | | 0.64 ^b [8] 0.24±0.02 [12] 0.54±0.11 ^d [This work] |
| Z-but-2-ene | 1.15±0.10 ^a [8] 1.19±0.14 [9] 0.94 [12] 0.86±0.03 ^c [This work] | | 0.41 ^b [10] 0.17±0.02 [12] 0.33±0.07 ^d [This work] |
| 2-methylbut-2-ene | 0.69±0.02 [8] 0.75±0.1 [9] 0.66±0.02° [This work] | 0.30±0.01 [8] 0.38±0.03 [9] 0.35±0.03° [This work] | 0.89 ^b [10] 0.93±0.14 [11] 0.81±0.16 ^d [This work] |

Table 1. Primary carbonyl and OH yields relative to alkene consumed in the reactions of ozone with alkenes

a, single value obtained from a mixture of *E*- and *Z*-but-2-ene; b, errors reported as a factor of 1.5; c, errors at 95 % confidence; d, errors reflect range of values observed.

3.1 Primary Carbonyl Yields

The formation of carbonyl compounds in each ozonolysis system was measured in the presence of a large excess of cyclohexane, which acted as a scavenger for OH radicals formed in the reactions; under the conditions of the experiments, more than 95 % of the OH radicals would be consumed by reaction with cyclohexane. Ethanal (acetaldehyde) was formed in the reaction of ozone with all three alkenes and propanone (acetone) was formed in the reaction of ozone with 2-methylbut-2-ene, as expected. The reported carbonyl yields were obtained from the slopes of plots of carbonyl concentration as a function of the change in alkene concentration. These plots were linear and gave the values quoted in table 1 directly.

3.2 OH Yields

Yields of hydroxyl radicals were determined by measuring the diminution in the concentration of TMB when in the presence of a reacting alkene-ozone system. The change in TMB concentration is given by

1208

$$\Delta[\text{TMB}] = \frac{k_1[\text{TMB}]}{k_1[\text{TMB}] + k_2[\text{Alkene}] + k_{\text{loss}}} \beta \Delta[O_3]$$
(I)

where k_1 is the rate constant for the reaction of OH with TMB, k_2 is the rate constant for the reaction of OH with alkene, k_{loss} describes the loss of OH in other processes, such as reaction with products, and β is the OH yield relative to ozone consumed. The three alkenes studied react rapidly with O₃ such that the amount of O₃ initially present reacts completely during the experiment. The apparent difficulty with using this simple analytical expression is that k_{loss} is variable and not usually known. For experiments with only a small addition of ozone, we expect this loss process to be commensurately very small; destruction of OH by reaction at walls and with ozone is much slower than loss by reaction with TMB and alkene, and reaction with products does not contribute significantly as these have not been formed in appreciable concentration. Therefore a plot of Δ [TMB] *vs*. Δ [O₃] for small additions of ozone is expected to be linear and to have a slope of βk_1 [TMB]_i/(k_1 [TMB]_i + k_2 [alkene]_i). What is observed experimentally (and is illustrated in figure 1), is that plots of [TMB] *vs*. Δ [O₃] are linear throughout the course of each experiment. The implication is that as the concentration of alkene is reduced through the reaction with ozone, k_{loss} increases as products are generated which can react with OH. Therefore, the slopes obtained from plots of [TMB] *vs*. Δ [O₃] were plotted as a function of k_1 [TMB]_i/(k_1 [TMB]_i + k_2 [alkene]_i) to yield linear plots with slope β , as illustrated in figure 2.



Figure 1: Experimental data for the ozonolysis of E-but-2-ene in the presence of TMB

The values of β derived from figure 2 are the OH yields relative to ozone consumed. Conversion to OH yields relative to alkene consumed is discussed later in the text.

Each alkene ozonolysis system was additionally analysed through the use of a numerical integrated model implemented using FACSIMILE [17]. The reaction scheme used to model the reaction of ozone with 2-methylbut-2-ene is shown schematically in figure 3. Although not included here, early models developed in this laboratory for the analysis of the ozonolysis of 2-methylbut-2-ene, in the presence of a scavenger, included the production of HO_2 via several decomposition channels. Reaction of HO_2 with O_3 can subsequently lead to additional OH radical production. However, because of the likely concentrations of the



Figure 2: Plot for analytical treatment of experimental results for 2-methylbut-2-ene (Δ), *E*-but-2-ene (\Box), *Z*-but-2-ene (O); where R = Δ [TMB]/ Δ [O₃]

intermediates involved, the fast self-reaction of HO₂ (compared with HO₂ + O₃) and the fact that the alkene is always in excess over ozone, formation of OH in this way is not significant in these experiments. Rate constants were taken from reference 18, the branching ratio, α , from this work, and β was varied to give the best fit between model and experimental data. Both TMB and alkene concentrations were used in this procedure, the best fit being determined by a least squares method. The model cannot fully describe the complex chemistry that goes on in this system; however, the reactions of OH with the alkenes used here and TMB are much faster than the reactions of OH with any likely products, and it seems reasonable to assume that the model can describe the OH chemistry that is relevant for the determination of OH yields. The results of the simulation are illustrated in figure 4.

The data shown in figures 2 and 4 indicate that the agreement between the two methods of analysis is very good, although the analytical method gives values for the OH yields between 2 and 6 % lower than the numerical method. The values quoted in the figures for β are the OH yields relative to ozone consumed. For Z- and E-but-2-ene, the yields relative to alkene are identical to those relative to ozone, because separate experiments in the presence of excess cyclohexane showed that the stoichiometry for the reactions of these two alkenes with ozone is unity. However, for 2-methylbut-2-ene, similar experiments showed that Δ [alkene]/ Δ [O₃] =1.20±0.05 (95% confidence). Therefore, the OH yields relative to 2-methylbut-2-ene consumed are given by β /1.2. It is not clear what the cause of this anomalous stoichiometric ratio is; it seems to indicate that there is a process occurring in the reaction of ozone with 2-methylbut-2-ene that is not understood. The values for the OH yields quoted in table 1 are the average of the yields relative to alkene consumed determined using the two methods of analysis.



Figure 3: Reaction scheme used to model the reaction of ozone with 2-methylbut-2-ene



Figure 4: Summary of modelled OH yields for 2-methylbut-2-ene (△), E-but-2-ene (□), Z-but-2-ene (O)

4. Discussion

The carbonyl yields measured in this study are in reasonable agreement with the results of other workers. Although our total primary carbonyl yields are at the low end of the range of previous measurements, all recent studies indicate that the total yield is close to unity, as expected on the basis of the accepted mechanism for alkene ozonolysis.

The hydroxyl radical yields obtained from this study are in very good agreement with the values of Atkinson and co-workers [10, 11], but are larger by about a factor of two than those of Gutbrod *et al* [12]. The cause of this discrepancy is not clear. What is certain is that the chemistry of the reactions of ozone with alkenes is complex, and is further complicated by the addition of an OH tracer/scavenger, whether it is cyclohexane [10], carbon monoxide [12], 2-butanol [11] or TMB as used in the current study. Gutbrod *et al.* [12] have argued that the secondary chemistry induced by the addition of carbon monoxide is likely to be less complex than that induced by the addition of more complex organic compounds. That is certainly true, but the

product they use to trace the OH yields (CO_2) is also a product of the reactions in the absence of added carbon monoxide, thus clouding the issue. It is possible that the addition of carbon monoxide, either directly or indirectly, interferes with the processes that generate carbon dioxide in the scavenger-free systems. The method used in the present study suffers from the problem that the tracer cannot be added in a sufficiently large concentration to react with all the hydroxyl radicals. However, the OH yields can be extracted from the experimental measurements by a simple analytical method to give values that agree with a numerical analysis and the yields do not show any strong dependence on the ratio of tracer-to-alkene concentration. Most importantly, this method is distinct from the others in that a different tracer/scavenger is used, changes in tracer concentration rather than product concentrations are measured and yields are determined over a range of tracer-to-alkene ratios.

What this study does not resolve unambiguously is the source of the hydroxyl radicals. It is assumed that they are formed *via* the direct decomposition of the Criegee intermediate, but it is clearly possible that other secondary chemistry may be involved. However, OH yields measured using three different types of scavenger — cyclohexane, 2-butanol and TMB — are in agreement for the reaction of ozone with 2-methylbut-2-ene, indicating that secondary chemistry induced by the scavenger is probably not important. Furthermore, in the present study, no systematic trends were observed over a range of [tracer] to [alkene] ratios. Finally, the yields determined by Atkinson and co-workers for a very wide range of compounds show systematic trends with structure that seem consistent with the hydroxyl radicals being generated in the direct decomposition of the Criegee intermediate.

5. Conclusions

The reactions of ozone with Z-but-2-ene, E-but-2-ene and 2-methylbut-2-ene under 'OH-free' conditions give total primary carbonyl yields close to unity, confirming the results of other investigations. The OH yields that we obtained for these reactions strongly support the high values previously reported by Atkinson and co-workers, our values being about a factor of two larger than those reported by Gutbrod *et al.*. Although the evidence is not conclusive, the present results add weight to the assumption that the OH radicals are generated directly in the decomposition of the Criegee intermediate.

6. Acknowledgements

The authors acknowledge the support of the Natural Environment Research Council under the Laboratory studies in Atmospheric Chemistry thematic programme. GM thanks the Research Board at the University of Reading for support to attend the Degradation Processes in the Environment meeting. DJ acknowledges the support of the EPSRC.

7. References

[1] R. Atkinson, and W. P. L. Carter, Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions, *Chem. Rev.*, 84. 437-470 (1984).

1212

[2] H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach and M. D. Hurley, FTIR spectroscopic study of the mechanism for the gas-phase reaction between ozone and tetramethylethylene, *J. Phys. Chem.*, **91**, 941-946 (1987).

[3] S. E. Paulson and J. J. Orlando, The reactions of ozone with alkenes: an important source of HO_x in the boundary layer, *Geophys. Res. Lett.*, **23**, 3727-3730 (1996).

[4] S. Hatakeyama, H. Kobayashi and H. Akimoto, Gas-phase oxidation of SO_2 in the ozone-olefin reactions, J. Phys. Chem., **88**, 4736-4739 (1984).

[5] R. A. Cox and S. A. Penkett, Aerosol formation from sulphur dioxide in the presence of ozone and olefinic hydrocarbons, *J. Chem. Soc.*, *Faraday Trans I*, **68**, 1735-1753 (1972).

[6] P. Neeb, F. Sauer, O. Horie and G. K. Moortgat, Formation of hydroxymethyl hydroperoxide and formic acid in alkene ozonolysis in the presence of water vapour, *Atmos. Environ*, **31**, 1417-1423 (1997).

[7] D. Grosjean, E. Grosjean and E. L. Williams II, Atmospheric chemistry of olefins - a product study of the ozone alkene reaction with cyclohexane added to scavenge OH, *Environ. Sci. Technol.*, **28**, 186-195 (1994).

[8] E. Grosjean, D. Grosjean and J. B. de Andrade, Carbonyl products of the gas-phase reaction of ozone with simple alkenes, *Environ. Sci. Technol.*, **30**, 975-983 (1996).

[9] E. C. Tuazon, S. M. Aschmann, J. Arey and R. Atkinson, Products of the gas-phase reaction of ozone with a series of methyl-substituted ethenes, *Environ. Sci. Technol.*, **31**, 3004-3009 (1997).

[10] R. Atkinson and S. M. Aschmann, OH radical production form the gas-phase reactions of ozone with a series of alkenes under atmospheric conditions, *Environ. Sci. Technol.*, **27**, 1357-1363 (1993).

[11] A. A. Chew and R. Atkinson, OH formation yields from the gas-phase reactions of ozone with alkenes and monoterpenes, *J. Geophys. Res.*, **101**, 28,649-28,653 (1996).

[12] R. Gutbrod, S. Meyer, M. M. Rahman and R. N. Schindler, On the use of CO as a scavenger for OH radicals in the ozonolysis of simple alkenes and isoprene, *Int. J. Chem. Kinet*, **29**, 717-723 (1997).

[13] C. Schäfer, O. Horie, J. N. Crowley and G. K. Moortgat, Is the hydroxyl radical formed in the gasphase ozonolysis of alkenes?, *Geophys. Res. Lett.*, **24**, 1611-1614 (1997).

[14] S. E. Pauslon, A. D. Sen, P. Liu, J. D. Fenske and M. J. Fox, Evidence for the formation of OH radicals from the reaction of O_3 with alkenes in the gas-phase, *Geophys. Res. Lett.*, **24**, 3193-3196 (1997).

[15] G. Marston, C. D. McGill and A. R. Rickard, Hydroxyl-radical formation in the gas-phase ozonolysis of 2-methylbut-2-ene, *Geophys. Res. Lett.*, **25**, 2177-2180 (1998).

[16] N. M. Donahue, J. H. Kroll, J. G. Anderson and K. L. Demerjian, Direct observation of OH production from the ozonolysis of olefins, *Geophys. Res. Lett.*, **25**, 59-62 (1998).

[17] E. M. Chance, A. R. Curtis, I. P. Jones and C. P. Kirby, Report AERE-R 8775, Atomic Energy Research Establishment, Harwell, U.K. (1997).

[18] R. Atkinson, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, *J. Phys. Chem. Ref. Data*, Monograph, 1:246pp (1989).