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Trimethylsilyl group migration in the Criegee intermediate of gas-phase ozonolysis of trimethylsilylethenes

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Abstract

GC, GC/MS and GC/FTIR analyses of the final products of ozonolysis of trimethylsilylethene and *trans*-1,3-bis(trimethylsilyl)ethene reveal that the ester channel of decomposition of the Criegee intermediate takes place exclusively via migration of Me₃Si group. © 2000 Elsevier Science Ltd. All rights reserved.

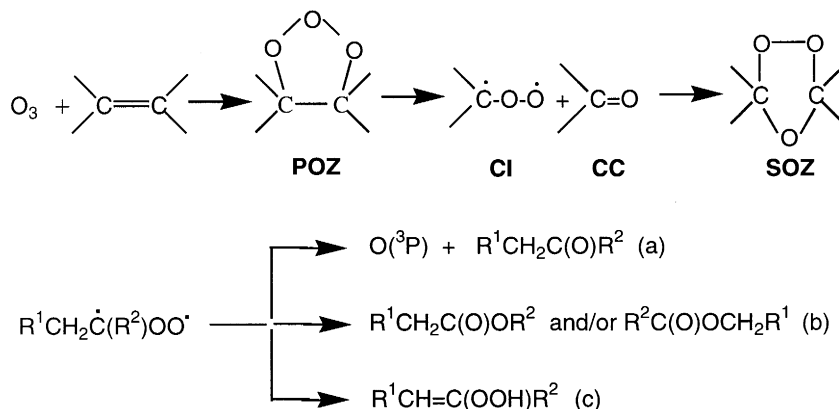
Keywords: ozonolysis; rearrangement; alkenes; silicon and compounds.

Much attention has been paid for over 40 years to the mechanism of the gas-phase ozonolysis of alkenes¹ and this topic was recently reviewed.² The ozonolysis of alkenes is a multi-step reaction and it proceeds via an unstable primary ozonide (POZ) which decomposes³ to a carbonyl compound (CC) and a carbonyl oxide diradical (referred to as the Criegee intermediate, CI). The latter species plays a pivotal role in the ensuing steps. Apart from its recombination with the geminal CC to a secondary ozonide (SOZ),⁴ it undergoes bimolecular reactions⁵ and decomposes via at least three different routes.⁶ These are O-atom elimination (a), the ester (b) and the hydroperoxide (c) channels. All these ozonolysis steps are illustrated in Scheme 1.

The decomposition channels afford a multitude of mostly lower molecular weight species. Their relevance is ascribed to the occurrence of unique indicator products⁶ and is dependent on the CI structure and ozonolysis conditions. Thus, the O(³P)-atom elimination channel is significant at low but not at atmospheric pressure^{2a} and the hydroperoxide channel, an important source of OH radicals, is favoured with *syn*-positioned methyl (alkyl) groups^{3a} and feasible only with H atom(s) at the carbon bonded directly to the C radical centre. As to the ester channel, it affords in principle two different rearranged products, but the present state of knowledge leaves considerable uncertainty on which group migration is preferred.

In conjunction with our previous studies on the gas-phase ozonolysis of alkenes^{4a,c} and the gas-phase decomposition of secondary ozonides,⁷ we address in this note the problem of the selectivity in the CI

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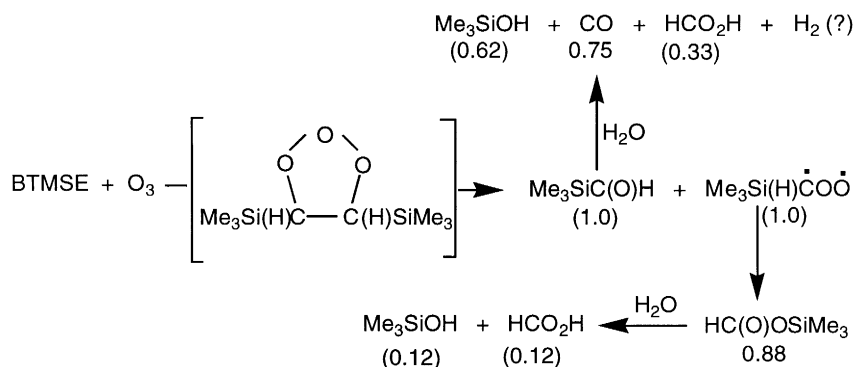


Scheme 1.

ester decomposition channel in the gas-phase ozonolysis of trimethylsilylethene (TMSE) and *trans*-1,3-bis(trimethylsilyl)ethene (BTMSE). With these compounds, the $O(^3P)$ -atom elimination channel will not be important at atmospheric pressure and the CI hydroperoxide channel will not be operative due to the absence of H atoms β to the C=C bond. This leaves the ester channel as the only route of the CI decomposition and trimethylsilyl formate and trimethylsilanecarboxylic acid as the respective indicator products of migration of the trimethylsilyl group and hydrogen. The analysis of the final products in the ozonolysis of TMSE and BTMSE can thus reveal the relative rate of migration of the H and the Me_3Si group in the CI diradical.

The ozonolysis was carried out by mixing ozone and the alkene (both in an excess of nitrogen).⁸ The progress of the ozonolysis was monitored by FTIR spectroscopy⁹ and the reaction mixture was analysed 30 min after mixing by gas chromatography, gas chromatography–mass spectrometry and gas chromatography–FTIR spectroscopy.¹⁰

The ozonolysis of BTMSE resulted in a 54% depletion of BTMSE and the formation (yield in mol/mol of BTMSE reacted) of trimethylsilyl formate (0.88), carbon monoxide (0.75), trimethylsilanol (0.74), formic acid (0.45), carbon dioxide (0.008) and hexamethyldisiloxane (0.003). The major products can be rationalised in terms of Scheme 2, where the POZ decomposes into the CI and the CC and where the tentatively assumed yields are given in brackets.

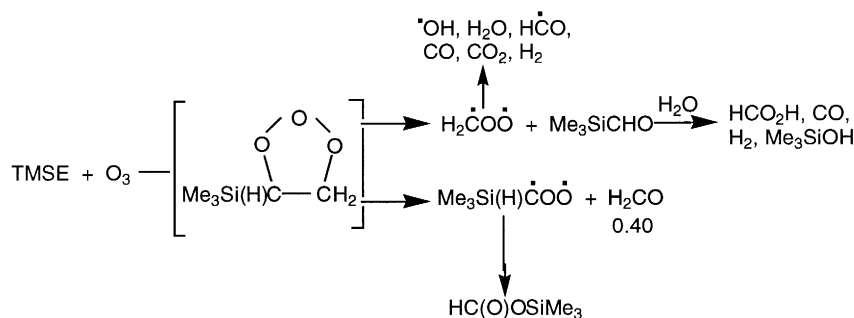


Scheme 2.

While the decomposition modes of the unstable¹² trimethylsilylformaldehyde (CC) are uncertain and may involve Si–C bond homolysis assisted with traces of water or the cell surface, the decomposition of trimethylsilylcarbonyl oxide diradical (CI) is unequivocally shown, through the high yield of trime-

thylsilyl formate and the absence of stable¹³ trimethylsilanecarboxylic acid, to take place via exclusive migration of the Me₃Si group and not of the hydrogen. Some deficiency for silicon cannot be, however, accounted for at present.

The ozonolysis of TMSE resulted in a 64% depletion of TMSE and yielded (in mol/mol of TMSE reacted) formaldehyde (0.40), carbon monoxide (0.39), trimethylsilanol (0.38), trimethylsilyl formate (0.25), hexamethyldisiloxane (0.16), formic acid (0.024), (hydroxy)pentamethyldisiloxane (0.01), hexamethylcyclotrisiloxane (0.003) and octamethyltrisiloxane (0.03). This ozonolysis is in keeping with the formation of the two pairs of CC and CI products (Scheme 3). Among the major final products, formaldehyde and trimethylsilyl formate can be identified as the primary CC product and the product of 1,3-Me₃Si group migration in the CI, respectively.



Scheme 3.

The absence of trimethylsilanecarboxylic acid is again in line with the absence of a 1,3-H shift in the CI. The smaller yield of trimethylsilyl formate and the higher yield of hexamethyldisiloxane, compared to those in the ozonolysis of BTMSE, are consistent with formation of water in this ozonolysis. The H₂COO diradical is known^{2a,6c,14} to decompose, aside from other routes, to H₂O+CO and HCO+OH. It is thus conceivable that the radicals so produced abstract H from the Me₃Si group and induce formation of dimethylsilene Me₂Si=CH₂ which adds H₂CO and affords¹⁵ dimethylsilanone Me₂Si=O. Only the occurrence of the latter transient can explain the formation of the observed (hydroxy)pentamethyldisiloxane and trisiloxanes, since the insertion of Me₂Si=O into the Si–O bond of trimethylsilanol and hexamethyldisiloxane, or its cyclotrimerisation affords these compounds.¹⁵ It is thus evident that although the terminal CH₂ group of the alkene causes the formation of more products, the ester channel of the CI decomposition is controlled by the migration of the Me₃Si group even in this case.

The 1,3-migration of the Me₃Si group in the Criegee intermediate adds to the class of rearrangements of diradicals¹⁶ and to the family of organosilicon carbon-functional species.¹⁷

Acknowledgements

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References

- (a) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437–470. (b) Kuczkowski, R. L. *Chem. Soc. Rev.* **1992**, 79–83. (c) Herron, J. T.; Martinez, R. I.; Huie, R. E. *Int. J. Chem. Kinet.* **1982**, *14*, 201–224. (d) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padva, A., Ed.; Wiley: New York, 1984; Vol. 2, Chapter 11. (e) Grosjean, D. *Environment. Sci. Technol.* **1990**, *24*, 1428–1432.

2. (a) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215–290. (b) Horie, O.; Moortgat, G. K. *Acc. Chem. Res.* **1998**, *31*, 387–396.
3. (a) Gutbrod, R.; Kraka, E.; Schindler, R. N.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7330–7342. (b) Ponec, R.; Yuzhakov, G.; Haas, Y.; Samuni, U. *J. Org. Chem.* **1997**, *62*, 2757–2762.
4. (a) Fajgar, R.; Vitek, J.; Haas, Y.; Pola, J. *Tetrahedron Lett.* **1996**, *37*, 3391–3394. (b) Horie, O.; Moortgat, G. K. *Tetrahedron Lett.* **1996**, *37*, 9297–9300. (c) Fajgar, R.; Vitek, J.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 239–248.
5. For example: (a) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1987**, *91*, 941–953. (b) Thamm, J.; Wolff, S.; Turner, W. V.; Gäb, S.; Thomas, W.; Zabel, F.; Fink, E. H.; Becker, K. H. *Chem. Phys. Lett.* **1996**, *258*, 155–158. (c) Neeb, P.; Horie, O.; Moortgat, G. K. *Chem. Phys. Lett.* **1995**, *246*, 150–156.
6. (a) Martinez, R. I.; Herron, J. T. *J. Phys. Chem.* **1988**, *92*, 4644–4648. (b) Martinez, R. I.; Herron, J. T. *J. Phys. Chem.* **1987**, *91*, 946–953. (c) Horie, O.; Moortgat, G. K. *Atmos. Environ., Part A* **1991**, *25*, 1881–1896.
7. (a) Khachatryan, L.; Fajgar, R.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1981–1984. (b) Khachatryan, L.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1147–1151.
8. Alkene (45 Pa) in 50 kPa of N₂, and ozone (135 Pa) in 150 kPa of N₂ were prepared each in a 2 l Pyrex flask equipped with PTFE valves and attached to a standard vacuum manifold. The quick opening and closing of the valve through which both flasks were interconnected equalised pressures in both flasks and allowed the ozonolysis between 45 Pa of the alkene and 45 Pa of ozone to proceed at ambient temperature at 100 kPa of N₂.
9. In situ FTIR spectroscopy absorption measurements were performed in cells with optical path length 20 cm or 1 m having respective volumes 250 ml and 1 l.
10. Gaseous samples for the GC analysis were withdrawn by a gas-tight syringe through a septum. The GC/MS and GC/FTIR analyses were conducted on total amounts of the ozonolysis products concentrated in a small ampoule attached to the vacuum-line and cooled with liquid nitrogen. The analyses by GC (FID) and GC/MS were conducted on a 3.3 m long column packed with 5% SE 30 on Chromosorb W. Response factors were determined (TMSE 0.70, BTMSE 0.65, hexamethyldisiloxane 0.52), taken from the literature,^{11a} or calculated^{11b} (trimethylsilanol 0.48, trimethylsilyl formate 0.47).
11. (a) Dietz, W. A. *J. Gas Chromatogr.* **1967**, *5*, 68–71. (b) Lee Smith, A. *The Analytical Chemistry of Silicon Compounds*; Wiley: New York, 1991.
12. (a) Sommer, L. H.; Bailey, D. L.; Goldberg, G. M.; Buck, C. E.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613–1618. (b) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198–2200. (c) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049–2056. (d) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84. (e) Trommer, M.; Sander, W. *Organometallics* **1996**, *15*, 189–193.
13. Steward, O. W.; Dzedzic, J. E.; Johnson, J. S. *J. Org. Chem.* **1971**, *36*, 3475–3480.
14. Su, F.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1980**, *84*, 239–246.
15. Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 17.
16. For example: (a) Freidlina, R. Kh.; Terent'ev, A. B. *Russ. Chem. Rev.* **1974**, *43*, 129–139. (b) March, J. *Advanced Organic Chemistry; Reactions, Mechanisms, and Structure*; Wiley: New York, 1985. (c) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1. (d) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, essay 5.
17. (a) Pola, J. In *Carbon-Functional Organosilicon Compounds*; Chvalovsky, V.; Bellama, J. M., Eds.; Plenum Press: New York, 1984. (b) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, essay 9. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 5.