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Trimethylsilyl Group Migrations in Cryogenic Ozonolysis of Trimethylsilylethene: Evidence for Nonconcerted Primary Ozonide Decomposition Pathway

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The identification of trimethylsiloxy-1,2-dioxetane and 2-trimethylsilyloperoxyacetaldehyde and assignment of trimethylsiloxymethyl formate as products of the low-temperature ozonolysis of trimethylsilylethene demonstrate feasibility of migrations of trimethylsilyl group in a dioxygen-centered (oxyperoxy) diradical produced via a homolytic cleavage of each of both O−O bonds in the primary ozonide. The results provide the first experimental evidence on the nonconcerted decomposition of the primary ozonide.

Introduction

The ozonolysis of alkenes is a complex reaction that proceeds via the Criegee mechanism[1] involving the primary ozonide (POZ), a carbonyl oxide (referred to as the Criegee intermediate, CI), a carbonyl compound (CC), and the secondary ozonide (SOZ) (Scheme 1).

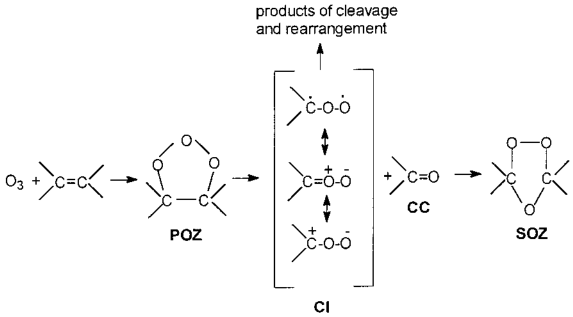
Theoretical work described the POZ as decomposing into the CI and CC kept in close proximity in a dipole complex.[2] Theoretical prediction claims that the CI singlet diradical structure is more stable than the zwitterionic one,[3] whereas experimental results[4] are in favor of a 1,3-dipolar molecule with a three-center, four-π-electron, 3p orbital system.

The experimental work showed that the final ozonolysis products depend on the alkene structure and on the reaction medium.

A large body of studies on the *gas-phase* ozonolysis of the alkenes aimed at determining importance of this reaction in atmosphere revealed the occurrence of several decomposition pathways of the energy-rich CI species,[5] the feasibility of the CC and CI combination to the SOZ in the absence of stabilizing effect of solvent,[6] and the insignificance of the SOZ decomposition.[7]

In extensive examinations of the ozonolysis in the *condensed phase*, secondary ozonides, aldehydes, ketones, carboxylic acids, hydroperoxides, and oligomers were revealed as the final products.[1] Unstable POZs were identified at low temperatures by NMR,[8] IR,[9] and microwave[10] spectroscopy and recognized[1c,11] as being formed via concerted cycloaddition of ozone to the alkene double bond. The preceding stages to the POZ, a van der Waals complex,[12] and a colored π-complex[9e] of ozone and alkene were also suggested.

Scheme 1. Criegee Mechanism of Alkene Ozonolysis



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(1) (a) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745−752. (b) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1; 1982; Vol. 2. (c) Kuczkowski, R. *Chem. Soc. Rev.* **1992**, 79−83.

(2) (a) Ponec, R.; Yuzhakov, Y.; Haas, Y.; Samuni, U. *J. Org. Chem.* **1997**, *62*, 2757−2762. (b) Gutbrod, R.; Kraka, E.; Schindler, R. N.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7330−7342.

(3) (a) Wadt, W. R.; Goddard, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 3004−3021. (b) Hiberty, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6088−6092.

(4) (a) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (b) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (c) Ishiguro, K.; Nojima, T.; Sawaki, Y. *J. Phys. Org. Chem.* **1997**, *10*, 787.

(5) (a) Horie, O.; Moortgat, G. K. *Acc. Chem. Res.* **1998**, *31*, 387−396. (b) Atkinson, R. *J. Phys. Chem., Ref. Data* **1997**, *26*, 215−290.

(6) (a) Fajgar, R.; Vitek, J.; Haas, Y.; Pola, J. *Tetrahedron Lett.* **1996**, *37*, 3391−3394. (b) Fajgar, R.; Vitek, J.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 239−248 and references therein.

(7) (a) Khachatryan, L.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1147−1151. (b) Khachatryan, L.; Fajgar, R.; Haas, Y.; Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1981−1984.

(8) (a) Durham, L. J.; Greenwood, F. L. *J. Org. Chem.* **1968**, *33*, 1629−1632. (b) Bailey, P. S.; Thompson, J. A.; Shoulders, B. A. *J. Am. Chem. Soc.* **1966**, *88*, 4098−4099. (c) Durham, L. J.; Greenwood, F. L. *J. Chem. Soc., Chem. Commun.* **1968**, 24−25.

(9) (a) Hull, L. A.; Hisatsune, I. C.; Heicklen, J. *J. Am. Chem. Soc.* **1972**, *94*, 4856−4864. (b) Nelander, B.; Nord L. *Tetrahedron Lett.* **1977**, *32*, 2821−2822. (c) Kohlmiller, C. K.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 2578−2582. (d) Alcock, W. G.; Mile, B. *J. Chem. Soc., Chem. Commun.* **1973**, 575−576. (e) Alcock, W. G.; Mile, B. *J. Chem. Soc., Chem. Commun.* **1976**, 5−6. (f) Mile, B.; Morris, G. W.; Allcock, W. G. *J. Chem. Soc., Perkin II* **1979**, 1644−1652. (g) Samuni, U.; Fraenkel, R.; Haas, Y.; Fajgar, R.; Pola, J. *J. Am. Chem. Soc.* **1996**, *118*, 3687−3693.

(10) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1988**, *110*, 7991−7999.

(11) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2, Chapter 1.

(12) Gillies, C. W.; Gillies, J. Z.; Suenram, R. D.; Lovas, F. J.; Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 2412−2421.

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Despite that data, the theoretically predicted mode of the POZ decomposition has not yet found any experimental support. Thus, the attempts to isolate the primary products at low temperatures revealed puzzling features explainable only by assuming an operation of a blend of substituent effect, a general medium effect, and a specific nucleophilic solvent assistance. These effects were surmised to be of different importance for different alkenes.[9f,13] Furthermore, the experimental evidence on concerted cycloreversion of the POZ into a pair of the CC and CI is considered inferential.[1c,11] This is due to the fact that the rationale constructed from the stereochemistry of ozonolysis with *cis*(*trans*)-1,2-alkenes is hampered by poor knowledge of the stereochemical properties of the CI.

We have previously examined[14] the gas-phase ozonolysis of trimethylsilyl-substituted ethenes and used the Me_3Si group as a tag to observe that the decomposition of the trimethylsilylated CI takes place exclusively via the ester[15] channel. The discovered migration ability of the Me_3Si group in the 1,3-diradical species spurred us to utilize this group in distinguishing among several O-function-containing ozonolysis intermediates trackable at low temperatures. Here, we report that the Me_3Si group migrations in low-temperature ozonolysis of trimethylsilylethene (TMSE) afford relatively stable trimethylsilyloxy-substituted products as unique indicators of the POZ decomposition routes and provide the first experimental evidence on the nonconcerted cycloreversion of the POZ in alkene ozonolysis.

Results and Discussion

The ozonolysis of TMSE was performed at different conditions in order to make analyses of reaction products possible by different techniques.

Co-Deposition of Ozone and TMSE into Xenon Matrix. The co-deposition of ozone and TMSE into xenon matrix at temperatures between −190 and −150 °C does not result in the ozonolysis of TMSE, since FTIR spectra of the matrix show only absorption bands of the reactants. New, very weak bands at 1731, 1696, 1314, 1205, 1174, 1124, and 1097 cm^{-1} start to appear only at −135 °C, but further temperature increase to −110 °C leads to xenon evaporation. At these conditions, TMSE depletion is very insignificant, since the ozonolysis begins only at ca. −140 °C when ozone diffuses from the Xe matrix.

Co-Deposition of Neat Ozone and TMSE. FTIR Spectral Studies. The co-deposition of ozone and TMSE without diluting xenon at −145 °C yielded films that when warmed to −130 °C showed the same FTIR spectral pattern as the films co-deposited with the Xe-diluted reactants (above). The FTIR spectrum of this film at −100 °C displays two carbonyl bands at 1736 and 1702 cm^{-1} (Figure 1a). Both ν(C=O) bands are observed already at the onset of the ozonolysis at the lowest temperature (−135 °C), whereas at −60 °C, the temperature at which some portion of the ozonolysis products evaporates, only that at 1736 cm^{-1} remains and the other is depleted (Figure 1b). This indicates that both ν(C=O) bands belong to different compounds. The FTIR spectral bands depleting at −60 °C are due to a compound that decomposes to formaldehyde (Figure 1d) and trimethylsilyl formate (**1**) (Figure 1e), as verified by measuring FTIR spectrum of products volatilized at −60 °C. We assume that H_2CO and **1** arise from the decomposition of the ozonolysis product possessing the ν(C=O) at 1702 cm^{-1}, which can be tentatively assigned as trimethylsilyloxymethyl formate (**2**), wherein the low ν(C=O) value is due[16] to the (p−d)σ C=O→Si interaction.

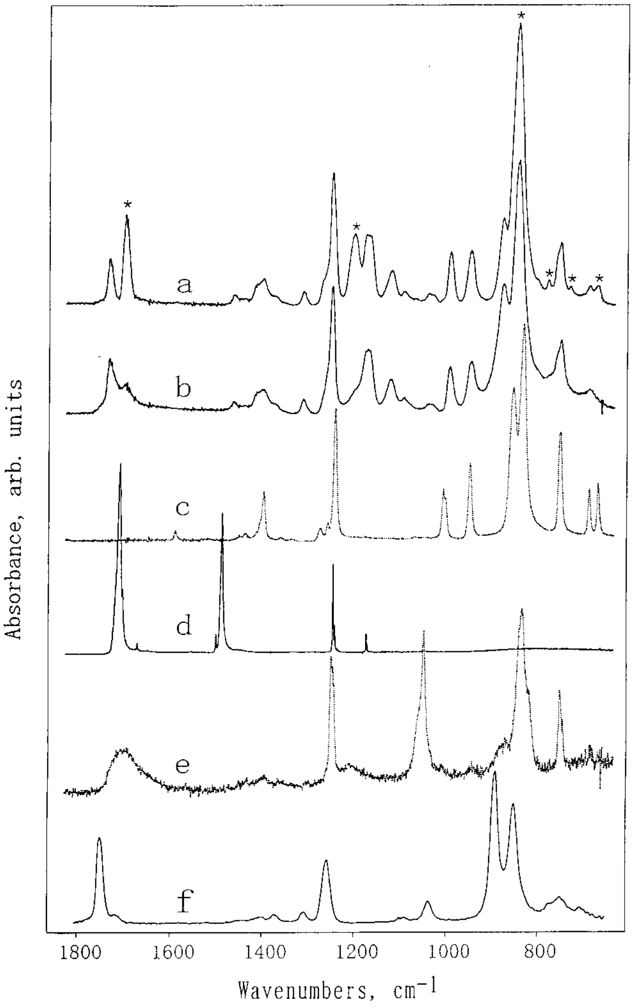

Figure 1. FTIR spectrum of TMSE − O_3 reaction at −100 °C (a) and −60 °C (b), TMSE (c, at −20 °C), formaldehyde (d, at −140 °C), trimethylsilyl formate (**1**) (e, at −120 °C), and 2-trimethylsilyloperoxyacetaldehyde (**3**) (f, at room temperature). The bands in (a) designated by an asterisk are tentatively assigned to trimethylsilyloxymethyl formate (**2**).

Mass Spectral Studies. The mass spectrum of the ozonolysis products evaporated at temperatures between −100 and −60 °C shows the fragmentation pattern [*m*/*z* (relative intensity)] 148 (1), 147 (7), 146 (7), 85 (27), 84 (100), 73 (10), 72 (10), 59 (56), 43 (17), 28 (28), while that of the products evaporated at temperatures higher than −60 °C shows the pattern [*m*/*z* (relative intensity)] 148 (16), 147 (100), 146 (72), 76 (10), 75 (41), 74 (22), 73 (10), 72 (10), 59 (10), 45 (14), 44 (30), 43 (11), 42 (20), 41 (11), 30 (19), 29 (31), 28 (30).

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(13) (a) Greenwood, F. L.; Durham, J. L. *J. Org. Chem.* **1969**, *34*, 3363−3366. (b) Greenwood, F. L. *J. Org. Chem.* **1965**, *30*, 3108−3111. (c) Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2197−2201 and refs. therein.

(14) Fajgar, R.; Pola, J. *Tetrahedron Lett.* **2000**, *41*, 2435−2438.

(15) (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.

(16) Pola, J.; Jakoubková, M.; Papoušková, Z.; Chvalovský, V. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1540−1550.

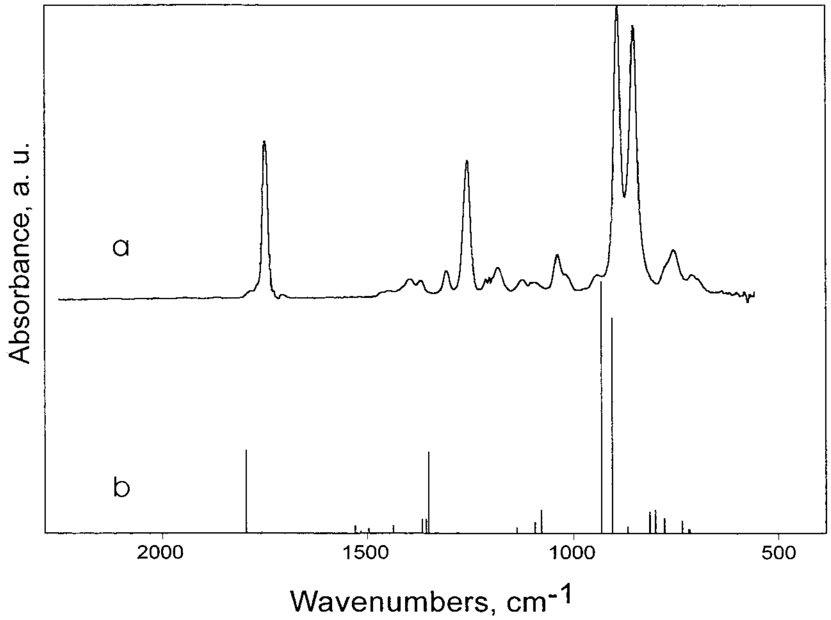

Figure 2. FTIR spectrum of $(CH_3)_3SiOOCH_2CHO$ (**3**): experimental, gas-phase (a); calculated (b).

Table 1. FTIR Spectrum of 2-Trimethylsilyloperoxyethan-1-one

experimental		calculated		assignment
frequency, cm^{-1}	intensity[a]	frequency, cm^{-1}	intensity[a]	
		257.26	0.04	
		287.84	0.05	
		345.88	0.10	
713	0.06	432.12	0.07	
754	0.16	734.64	0.05	ν(SiO)
775		777.11	0.06	
854	0.92	798.49	0.09	
892	1.00	813.78	0.09	
944	0.07	907.13	0.44	
1019	0.07	910.81	0.40	$\nu(CH_2O_{perox})$
1040	0.14	933.52	1.00	ν(OO)
1095	0.04	1078.12	0.09	
1126	0.05	1093.27	0.04	
1184	0.09	1350.33	0.16	
1260	0.45	1352.43	0.16	$\delta(SiCH_3)$
1312	0.08	1359.02	0.06	
1374	0.05	1368.45	0.06	
1401	0.05	1438.28	0.03	
		1530.68	0.03	
1752	0.53	1795.68	0.33	ν(C=O)
2819	0.09	3079.20	0.22	$\nu_s(CH_2)$
2912	0.08	3119.97	0.04	
2967	0.20	3191.61	0.03	
		3231.50	0.04	

[a] Normalized to the most intensive bands.

The latter is in keeping with molecules of the formulas $SiC_5H_{12}O_3$ reflecting the mass of ozone−TMSE products.

NMR Spectral Studies. The ozonolysis carried out in an NMR tube at −120 °C resulted in a mixture from which a portion distilled upon warming to −20 °C was identified as 2-trimethylsilyloperoxyacetaldehyde $(CH_3)_3SiOOCH_2CHO$ (**3**) [δ 9.90 (t, $J = 1.8$, 1H), δ 4.39 (d, $J = 1.8$, 2H), δ 0.245 (s, 9H)]. The NMR measurement of the mixture at −60 °C allowed identification of trimethylsiloxy-1,2-dioxetane (**4**) [δ 6.63 (t, $J = 5.2$, 1H), δ 5.50 (dd, $J = 5.2$, 5.6, 1H), δ 5.14 (t, $J = 5.6$, 1H), δ 0.22 (s, 9H)]. It also revealed weak signals at δ 5.28 and 9.83 (both s) assignable to HC(O) and OCH_2O hydrogens in the compound **2**.

Compound **4** could not be isolated, since it decomposed during distillation at −20 °C. Compound **3** is stable at room temperature for several hours.

Characterization of Compound 3. Compound **3** was further characterized by its mass spectrum at −40 °C [[m/z (relative intensity)] 148 (15), 147 (100), 146 (77), 131 (2), 75 (40), 74 (21), 73 (10), 72 (7), 66 (11), 59 (10), 45 (13), 44 (31), 43 (10), 42 (21), 41 (11), 30 (17), 29 (30), 28 (30)] and by its FTIR spectrum [[(wavenumber/cm^{-1} (relative absorptivity)[2965 (0.19), 2913 (0.09), 2819 (0.12), 1752 (0.57), 1310 (0.07), 1259 (0.42), 1099 (0.04), 1039 (0.12), 892 (1.00), 852 (0.77), 751 (0.15) (Figure 1f)] after distillation of the compound from the ozonolysis mixture into the spectroscopic cell at −20 °C. The assignment of the $(CH_3)_3SiOOCH_2CHO$ molecule is supported by the calculated IR vibrational frequencies and relative intensities (Table 1, Figure 2), which coincide well with the experimental values.

Mechanism. The products observed in this work are similar to trimethylsilyl acetate, trimethyl(trimethylsiloxy)-1,2-dioxetane, and 3-methyl-3-trimethylsilyloperoxybutan-2-one, which, being more stable than their nonmethylated counterparts, were identified in the ozonolysis of the "fully methylated" trimethyl(1,2-dimethyl-1-propenyl)silane in methylene chloride at −5 °C and assumed not to be formed in a one-step process.[17]

The spectral changes observed upon warming the cryogenically deposited TMSE and ozone allow us to assess initial stages of the reaction. The same pattern of the IR spectra (especially of the ν(C=O) bands) of the ozonolysis mixture at cryogenic temperatures in Xe and without it indicated that possible intermolecular pathways[4a,c] are not important. The intermolecular pathways would have been especially feasible[4a] with the CI. If liberated, $Me_3Si(H)COO$ (CI) would have undergone, e.g., cycloaddition[4a] to trimethylsilylethene, reaction[1b] with CC (H_2CO and Me_3SiCHO) to the SOZ, and two cross SOZs, and also O atom transfer reaction[4a] to $Me_3Si(H)C(O)$

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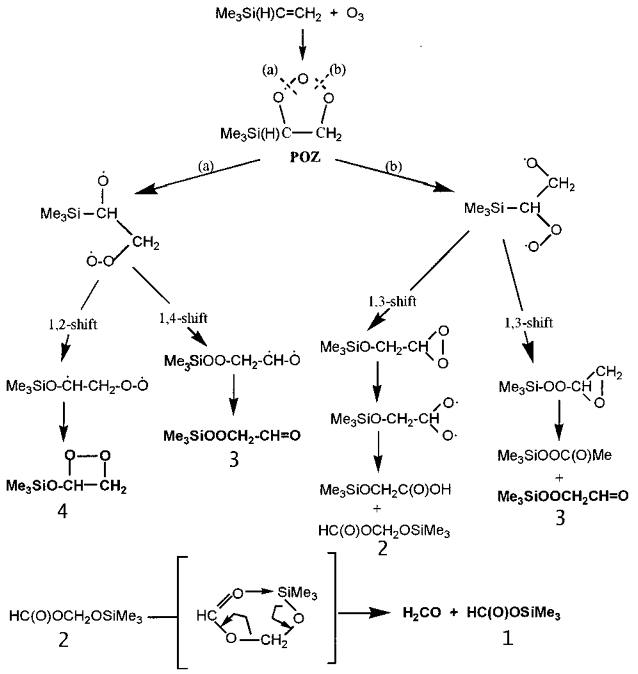
[17] Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1978**, *100*, 294.

Scheme 2. Diradical Mechanism of TMSE Ozonolysis



[ν(C=O) 1661 cm^{-1}, ref 18]. The fact that these products were not observed opposes to the transient occurrence of the CI, and also the occurrence of intermolecular steps, and suggests the operation of another mechanism.

We propose that the observed formaldehyde, compounds **1** and **3**, and the tentatively assigned compound **2** provide the first experimental evidence for the non-concerted nature of the POZ cleavage. Their formation can be only rationalized through a mechanism involving a homolysis of the O–O bonds in the POZ to yield two biradical intermediates that undergo intramolecular Me$_3$-Si-group transfer to both oxy and peroxy radical centers with subsequent ring closures, dioxirane ester-type rearrangements,[15] and carbonyl compounds formation from oxiranes.[19] These steps are depicted in Scheme 2, which describes no discrimination for migrations of the Me$_3$Si group to the O centers. Path a is supported by the occurrence of the compounds **3** and **4**, whereas the path b leading to unobserved Me$_3$SiOCH$_2$C(O)OH and Me$_3$-SiOOC(O)Me products may not appear substantiated. However, it is difficult to rationalize the occurrence of only one of the two paths and the existence of the 1,2 and 1,4- but not 1,3-Si shifts. We admit that the unknown (unstable) Me$_3$SiOCH$_2$C(O)OH compound should instantly decompose, and the unknown Me$_3$SiOOC(O)Me compound [analogous lit.[20] Me$_3$COOC(O)Me δ 1.98 (s, 3H)) could escape detection due to its low yield.

We note that most rearrangements of silicon-containing compounds are preferably explained as involving nucleophilic attack on silicon by the lone-pair electrons of adjacent more electronegative atom,[21] but reactions involving electron-deficient systems[22] can be exceptions.

We also remark that similar O–O homolytic pathway was suggested for the gas-phase decomposition of the POZ more than 25 years ago by Blumstein and O'Neal.[23] They described that thermochemical and kinetics requirements favor the O–O homolytic scheme involving H (and not Me$_3$Si-group) migrations over the Criegee decomposition mode into the pair of the CI and CC. However, the absence of experimental evidence as the failures to detect radicals by ESR technique,[23] or the absence of dicarbonyl and keto-hydroperoxide products (possibly due to their involvements in production of oligomers) made this proposal not having been given much attention. We do not stress that the diradical scheme for the POZ decomposition invoked in this work is generally applicable, since the ozonolysis is a multitude of competing reactions affected by many factors (solvent, temperature, alkene structure, pressure). We believe, however, that this pathway is of some feasibility at many conditions and that our results will improve understanding of many puzzling features,[1c,9f,11,13] which still wait for explanation.

Experimental Section

Reactants and Authentic Samples. The ozone was prepared in a 250 mL glass reactor furnished with PTFE stopcocks by applying a high-voltage discharge to 3.5 kPa of oxygen (Technoplyn, purity 99%). The yield of ozone was determined by FTIR spectroscopy using the diagnostic absorption band at 1053 cm^{-1}, and the excess of oxygen was removed by evacuating the vessel at −190 °C. TMSE was from the laboratory stock, and its purity was better than 98% as checked by gas chromatography. An authentic sample of trimethylsilyl formate (**1**) was prepared by ozonolysis of TMSE at −100 °C and obtained by distillation at −20 °C; its purity was checked by GC, and its FTIR and mass spectra agreed with literature.[24] Formaldehyde was prepared by heating paraformaldehyde under vacuum.

Co-Deposition of TMSE and Ozone in Cryogenic System. The ozonolysis of TMSE with and without diluting xenon was conducted in the cryogenic system and vacuum vessel (Figure 3) similar to those described in our previous studies.[9g] The co-deposition of ozone and of TMSE (each in a 50-fold excess of Xe) was performed at temperatures between −190 and −150 °C. Thereafter, the formed matrix was slowly warmed to −135 and to −110 °C at which temperatures FTIR spectra were recorded. In the co-deposition experiments without xenon, a thin layer of TMSE was deposited on the cryostat window at −145 °C when the FTIR spectrum of TMSE showed the narrowest bands. Thereafter, ozone was admitted via a capillary tubing and then the cell was slowly warmed. The FTIR spectra of the resulting film were recorded at several temperatures between −135 and −60 °C. The progress of the ozonolysis was followed at the diagnostic bands of TMSE at 1007.4 and 692.2 cm^{-1}, which were not overlapped with new absorption bands of ozonolysis products. Weak absorption

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[18] Trommer, M.; Sander, W.; Patyk, A. *J. Am. Chem. Soc.* **1993**, *115*, 11775–11783.

[19] (a) Braslavsky, S.; Heicklen, J. *Chem. Rev.* **1977**, *77*, 473–511. (b) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980.

[20] Nishinaga, A.; Nakamura, K.; Matsuura, T. *J. Org. Chem.* **1983**, *48*, 3696–3700.

[21] (a) Pola, J. In *Carbon-functional Organosilicon Compounds*; Chvalovsky, V., Bellama, J. M., Eds.; Plenum Press: New York, 1984. (b) Colvin, F. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 5. (c) 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.

[22] See, for example: (a) Freidlina, R. Kh.; Terentèv, 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.

[23] O'Neal, H. E.; Blumstein, C. *Int. J. Chem. Kinet.* **1973**, *5*, 397–413.

[24] Voronkov, M. G.; Yarosh, O. G. *J. General Chem.* (*U.S.S.R.*) **1972**, *42*, 2027–2029.

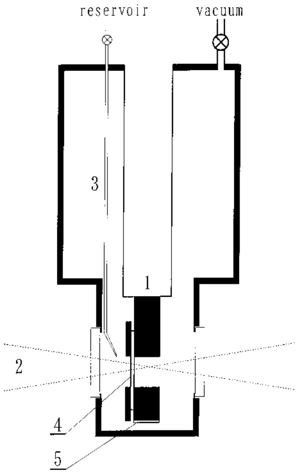

Figure 3. Cryogenic system: (1) copper finger cooled with liquid nitrogen; (2) FTIR spectrometer radiation; (3) capillary for introducing TMSE/N_2 and O_3/N_2 mixtures; (4) 2 mm thick NaCl window; (5) Pt thermometer.

bands of the ozonolysis products observed at −135 °C grew stronger at −120 and −110 °C. The spectra of pure ozonolysis products were obtained after further warming of the cell to −100 or −90 °C, at which temperatures TMSE was completely evaporated. The next warming of the cell to −60 °C led to the evaporation of some ozonolysis products as indicated by the depletion of several absorption bands.

Co-Deposition of TMSE and Ozone in Vessel. The ozonolysis of TMSE was also performed at −120 °C in a small glass evacuated vessel (5 mL in volume) in which TMSE was first condensed and then ozone was co-condensed in an amount sufficient to react with all the deposited TMSE. Several cycles were applied, and then the resulting mixture was evacuated at −90 °C and warmed to −60 °C, at which temperature some ozonolysis products evaporated and were frozen in an ampule by liquid nitrogen for FTIR analysis.

The ozonolysis of TMSE at −120 °C in the small glass vessel connected to the direct inlet of a mass spectrometer (the interconnection kept −60 °C) and subsequent warming to −60 °C allowed volatile ozonolysis products to be characterized by mass spectrometry.

The same procedure at −120 °C in an NMR tube afforded products that were after dilution with acetone-d_6 measured at −60 °C by NMR spectroscopy.

All spectra were recorded on an FTIR (Nicolet, model Impact 400) spectrometer, a GC−MS (Shimadzu, model QP 1000 quadrupole) spectrometer, ionizing voltage 70 eV), and an NMR (model Varian Unity 200, room temperature solvent $CDCl_3$, low-temperature solvent acetone-d_6, internal standard hexamethyldisilane, $\delta = 0.04$) spectrometer.

Ab initio calculation of the IR spectrum of $(CH_3)_3SiOOCH_2$-CHO molecule (**3**) was carried out using PCGAMESS program at the HF level with a 6-31G** basis set and complete energy optimization. Vibrational frequencies were calculated from the Hessian matrix using the harmonic approximation at the optimized geometries. The resulting frequencies were not scaled.

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Supporting Information Available: Energies and Cartesian coordinates for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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