

Laser-photosensitized homogeneous decomposition of 3,5-dimethyl-1,2,4-trioxolane: the evidence for intermediacy of products of rearrangement

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IR laser photosensitized (SF₆) decomposition of 3,5-dimethyl-1,2,4-trioxolane (DMTO) in the gas phase yields acetic acid, acetaldehyde, 1-hydroxyethyl acetate, 1-methoxyethyl formate and high molecular mass solid products. The formation of esters provides evidence for the 1,4-H and 1,4-Me shift taking place after the initial O–O bond split in DMTO, confirming a previously postulated intermediate for the decomposition of secondary ozonides. The products reveal that the homogeneous decomposition of DMTO is more complex than previously postulated for the decomposition in the liquid- and gas-phase.

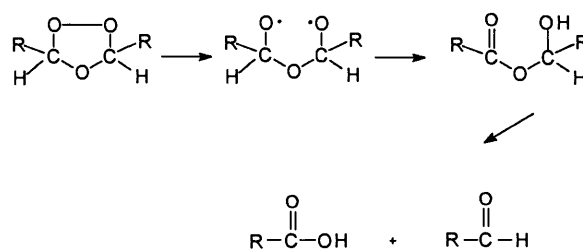
Introduction

The ozonation of olefins in the gas phase is of importance in atmospheric chemistry, but its detailed mechanism, despite extensive and continuing effort, is still awaiting complete understanding.¹ The prevailing view is that the initial steps are cycloaddition of ozone to olefins affording primary ozonide (POZ) and decomposition of POZ into a carbonyl compound and vibrationally excited carbonyl oxide (COX). Further reaction modes of COX, are reflected in a multitude of final products, which very much depend on the structure of COX and the reaction conditions.² One of the major points of interest is the occurrence (and reactions) of secondary ozonide (SOZ),³ the species formed by reaction of a carbonyl compound and COX. This plausible, and possibly important, intermediate can significantly contribute to the formation of the observed final products, but easily escapes detection. Though identified in low-temperature matrices and in solution, it was detected but not convincingly, nor conclusively, identified in rare instances in the gas phase,⁴ which may be due to its formation in a vibrationally excited state facilitating very fast decomposition.

For the assessment of the role of SOZ in olefin ozonation, a detailed knowledge of SOZ decomposition is required. The only paper on the gas phase decomposition of SOZs⁵ reported relatively low Arrhenius parameters thought to be inconsistent with a peroxide O–O bond scission and accounted for by a mechanism involving a highly ordered transition state in which the O–O bond cleaves simultaneously with H-atom transfer to yield equal amounts of carboxylic acid and aldehyde (Scheme 1). The postulated intermediates of the SOZ rearrangement have, however, been detected neither in the gas,⁵ nor in the liquid⁶ phase, which makes the postulated mechanism uncertain.

An alternative explanation of the low Arrhenius parameters might involve the contribution of surface catalysis. Heterogeneous steps, proved for many gas-phase reactions,⁷ are sometimes very difficult to avoid and an authentic homogeneous mechanism remains hidden from the observer. The truly homogeneous course of chemical reactions, which can be induced by radiation with CO₂ lasers,⁸ proceeds with a different course from conventional thermolysis⁹ and is useful for trapping intermediates.¹⁰

In this paper, we report on TEA CO₂ laser-induced homogeneous decomposition of DMTO and demonstrate its dissimilarity from conventional decomposition⁵ by revealing



Scheme 1

that the ratio of MeCO₂H and MeCHO products is very different from that observed in conventional decomposition. Furthermore, we describe the occurrence of the two hitherto unreported different products of rearrangement of DMTO, and lend strong support for the earlier postulated^{5,6} mechanism of the decomposition of secondary ozonides in the gas phase.

Experimental

All experiments were carried out using a grating-tuned TEA CO₂ laser (a 1300 M model, P. Hilendarski, Plovdiv University) operated on the P(20) (944.19 cm⁻¹) or P(28) line (936.8 cm⁻¹) of the 00⁰1 → 1⁰0 transition as confirmed by a model 16-A spectrum analyser (Optical Engineering Co.). These wavelengths were selected to achieve efficient absorption in sensitizing sulfur hexafluoride. The energy of the beam at each wavelength was 0.6 or 1.0 J per pulse. Irradiation of DMTO (0.1–0.2 kPa)–SF₆ (0.05–0.2 kPa)–N₂ (0–45 kPa) with a repetition rate of 1 Hz was conducted in a cylindrical (3.6 cm int. diameter, 11 cm long) Pyrex cell furnished with two NaCl windows and a PTFE stopcock used for filling and evacuating the vessel. The mixtures were introduced into the cell from a standard vacuum manifold and pressures of each component were measured by an Edwards pressure gauge and checked by an FTIR Nicolet Impact spectrometer. The changes in the composition of the irradiated mixtures were monitored by FTIR and GC–MS (Shimadzu QP 1000 quadrupole mass spectrometer) spectrometry as well as by GC (a GC 14 A Shimadzu gas chromatograph equipped with FID, a C-R5A Chromatopac computing integrator, columns packed with Porapak P (1.5 m), silicone elastomer SE-30 (3.3 m), and 5% 2,2'-oxydipropionitrile (3.3

Table 1 Main products of the DMTO decomposition

Irradiation line	Pressure/kPa			Energy in pulse J	Yield ^a of products (mol%)			
	DMTO	SF ₆	N ₂		MeCHO	MeCO ₂ H	CH ₂ CO ^b	MeCHO:MeCO ₂ H
P(28)	0.21	0.04	—	0.6	55	13	< 5	4.3
P(20)	0.18	0.12	8.00	1.0	62	13	—	4.7
P(20)	0.13	0.45	49.20	1.0	58	10	< 3	5.7

^a Based on converted DMTO. ^b Formed at later stages of decomposition (>40%).

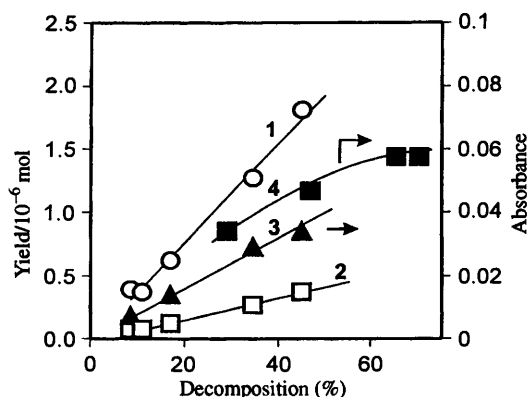


Fig. 1 Distribution of MeCHO (1), MeCO₂H (2) and compounds X + Y + Z (3,4) in the laser induced decomposition of DMTO. Curves 1–3 relate to DMTO (0.18 kPa)–SF₆ (0.10 kPa)–N₂ (8 kPa) and 1 J/pulse, curve 4 relates to DMTO (0.21 kPa)–SF₆ (0.1 Pa)–N₂ (8 kPa) and 0.5 J/pulse.

m]). The depletion of DMTO was monitored at 1228 cm⁻¹ and the gaseous products of the DMTO decomposition were identified by their IR spectra and MS. The formation of acetaldehyde, acetic acid and ketene was observed at 2730, 1292 and 2162 cm⁻¹, respectively. Pressures of the depleted DMTO and the other products were calculated from the determined optical densities of authentic samples at the above wavelengths.

DMTO was prepared by the ozonation of solid (*E*)-but-2-ene at -125 °C and purified from oligomeric substances by trap to trap distillations at 0.01 kPa, the traps being kept first at ambient temperature and -196 °C, and then at -50 °C and -196 °C. This procedure afforded DMTO in a purity of about 95% as checked by GC and GC-MS. Sulfur hexafluoride (Fluka) was degassed prior to use. Reference samples used for the analyses (acetic acid, acetaldehyde and ketene) of the DMTO decomposition were available from our laboratory stock.

Results and discussion

During the irradiation of the DMTO–SF₆–N₂ mixtures with the TEA CO₂ laser the laser energy is absorbed in highly stable sulfur hexafluoride and conveyed⁸ through molecular collisions to DMTO. The process affords acetaldehyde and acetic acid as the major products along with traces of ketene, methane, carbon dioxide, formic acid and methanol. The ratio of the two major products MeCHO:MeCO₂H, under different irradiation conditions and with different decomposition progress, is 4–6 (Table 1, Fig. 1), which is remarkably different from the equal amounts of these products observed with conventional thermal decomposition of DMTO.⁵

Typical IR absorbance spectra of the DMTO–SF₆ mixture before and after laser irradiation are displayed in Fig. 2, wherein depletion of absorption bands of DMTO at 1128 cm⁻¹ is accompanied by the development of new absorption bands for MeCHO (2730 cm⁻¹) and MeCO₂H (1292 cm⁻¹). The residual spectrum [Fig. 2(c)] derived from Fig. 2(b) by subtracting the spectral contributions of the DMTO, MeCHO, SF₆ and MeCO₂H shows several relatively broad bands which lack rotational fine structure and are characteristic of large

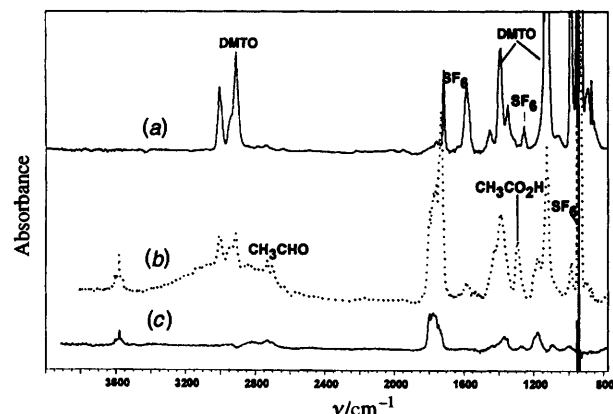


Fig. 2 IR spectrum of DMTO (0.18 kPa)–SF₆ (0.1 kPa)–N₂ (8 kPa) (a) before and (b) after irradiation, (c) residual spectrum obtained from (b) by subtracting DMTO, SF₆, acetic acid and acetaldehyde (a, b and c possess different ordinate scales).

molecules. Their band wavenumbers can be tentatively assigned as follows: 1002 cm⁻¹, 1093 cm⁻¹, 1176 cm⁻¹ (ν_{C–O}), 1274 cm⁻¹, 1369 cm⁻¹ (both δ_{C–CH₃}), 1774 and 1795 cm⁻¹ (ν_{C=O}), 2725 cm⁻¹, 2833 cm⁻¹ (both ν_{CH}) and 3590 cm⁻¹ (ν_{OH}). This residual spectrum exhibits the same pattern regardless of the decomposition range and different initial DMTO:SF₆ ratio. All these bands initially increase and reach a maximum value with the decomposition progress around 80%. This is illustrated for the band at 1795 cm⁻¹ in Fig. 2. A typical GC-MS trace of the products of the DMTO decomposition (Fig. 3) shows four peaks DMTO, X, Y and Z, possessing molecular ions at *m/z* 104 (DMTO, X and Y) and 118 (Z). These products show a mass fragmentation pattern [*m/z* (relative intensity)]: X 104 (1), 103 (13), 73 (58), 45 (100), 29 (32); Y 104 (1), 103 (10), 73 (40), 47 (17), 45 (100), 29 (22); Z 118 (1), 103 (2), 73 (23), 45 (61), 43 (100), 29 (18)] similar to DMTO [104 (4), 89 (15), 73 (3), 43 (100), 31 (13), 29 (32)] (for DMTO see ref. 11)]. The X and Y products are readily assigned to 1-hydroxyethyl acetate and 1-methoxyethyl formate, respectively, while the Z compound can be only tentatively assumed to have the structure [MeC(O)O]₂.

We note that similar esters, 1-hydroxyethyl¹² and hydroxy-methyl¹³ formates, were detected and identified by IR spectroscopy as products of (*E*)-but-2-ene and ethene gas-phase ozonation.

Two more facts are worth mentioning. The distribution of the observed products is not affected by addition of efficient chemical traps¹⁴ of COX like ethoxyethene or methanol. These experiments were carried out by laser irradiation of DMTO (0.2 kPa)–SF₆ (0.9 kPa)–trapping compound (5.5 kPa). Furthermore, we observed that neither acetaldehyde nor acetic acid decompose under the irradiation conditions used.

The observed compounds allow us to rationalize the homogeneous DMTO decomposition as a complex reaction scheme (Scheme 2). The initial cleavage of the weakest peroxide O–O bond affords the oxygens-centred biradical (I) (step i), as well as the 1,4-H-rearrangement (step iii) which were postulated previously on the basis of the kinetics of the decomposition⁵ and the observation of the final RCO₂H and RCHO products.⁶ The intermediate 1-hydroxyethyl acetate and 1-methoxyethyl

formate give evidence that I undergoes both 1,4 shift of H (step iii) and 1,4 shift of the Me group (step ii). Both esters may undergo decomposition (steps v and vii), or an oxidative decay (step vi) proceeding *via* their reaction with oxygen-transferring methyldioxirane¹⁵ produced by the β -cleavage of I (step iv).

Comparing the mode of decomposition of both 1-hydroxyethyl acetate and 1-methoxyethyl formate, of which the former has not been isolated until now and which was characterized only by NMR spectroscopy,¹⁶ that of 1-hydroxyethyl acetate (step vii, part of the previously postulated route^{5,6} for conventional thermal decomposition of secondary ozonides) into MeCO_2H and MeCHO should involve an elimination of HO-C(H)=CH_2 and its rearrangement into MeCHO , rather than cleavage of the C-O bond and a shift of H from OH to the forming MeCO_2 moiety. The latter decomposition mode with 1-methoxyethyl formate would yield HCO_2H and MeO(H)-C=CH_2 but this and any other envisagable modes lack support

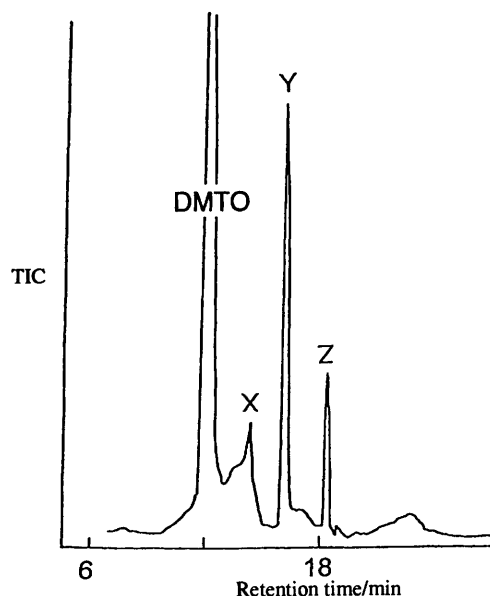


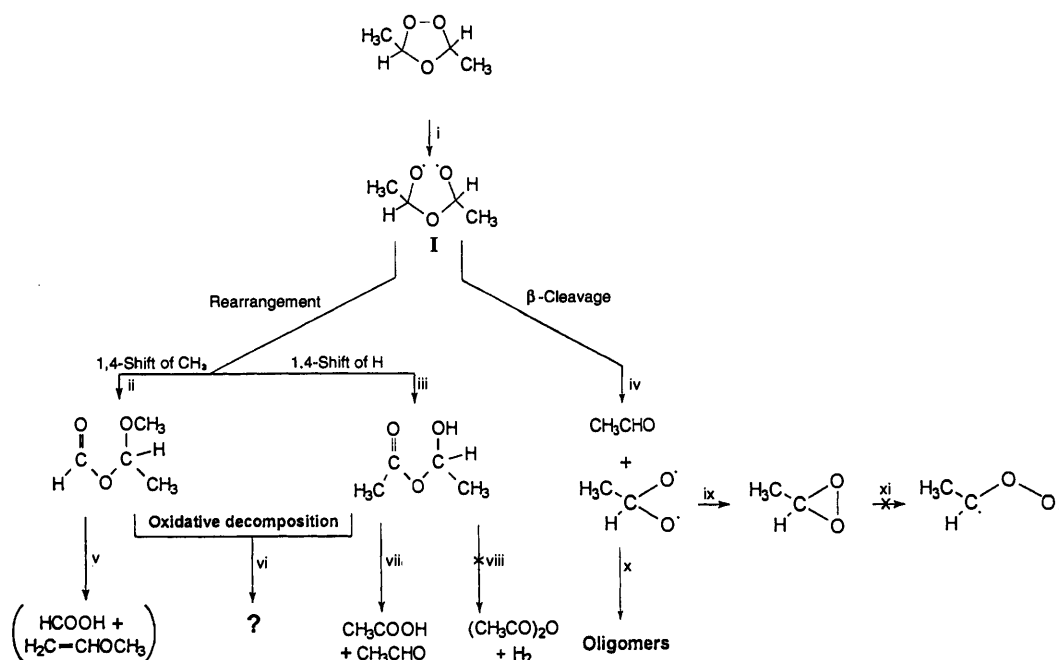
Fig. 3 Part of typical total ion current (TIC) trace for the GC-MS of the irradiated DMTO-SF₆-N₂ mixture. Column SE 30, programmed (15–150 °C) temperature.

from final products. We assume that step vii (yielding equal amounts of MeCHO and MeCO_2H) can be the only route affording acetic acid.

We remark that a dehydrogenative route of HOCH(Me)O-COME into H_2 and $(\text{MeCO})_2\text{O}$, similar to that reported earlier for hydroxymethyl^{13b,c} and 1-hydroxyethyl¹² formate decomposition during ozonation of ethene, can be ruled out because of the absence of acetic anhydride among the products. This is in agreement with the proved heterogeneous nature of this reaction.^{13b,c}

The high molar yield of MeCHO (>60%) and the $\text{MeCHO}:\text{MeCO}_2\text{H}$ ratio 4–6 imply that β -cleavage of the primary diradical into methylmethylenebis(oxyl) (step iv) is an important channel. We presume that methylmethylenebis(oxyl) may react by ring closure to methyldioxirane (step ix) but undergoes neither energetically demanding isomerization into the non-interconverting¹⁵ species COX (step xi) nor reaction(s) with MeCHO giving the observed esters. Two facts are in favour of such assumptions. (i) The absence of $\text{Me(H)\dot{C}-O-O\cdot}$ is supported by the absence of products¹⁴ of its reaction with the added ethoxyethene and methanol. (ii) The bimolecular production of the esters is less probable; it was observed^{3a} and interpreted as a quasi-concerted addition of vibrationally stabilized MeCHO_2 ¹⁶ or CH_2CO_2 ¹³ onto CH_2O , but not observed with methylenebis(oxyl)s and MeCHO .¹²

The occurrence of methylmethylenebis(oxyl) and methyldioxirane helps us to understand the low yields of MeCO_2H . Acetic acid might have been produced in high yields *via* the rearrangement of the methylmethylenebis(oxyl) (ester channel).¹⁷ We might have assumed that this route is hidden due to the decomposition into low molecular mass products like CO_2 , CH_4 , MeOH and $\text{CH}_2=\text{C=O}$ of methyldioxirane, methylmethylenebis(oxyl) or a hot acetic acid.^{3a,d,18} Very low MeCO_2H yields in the ozonation of (*E*)-but-2-ene are also due to such decompositions.^{3d,12} The observed occurrence of very minor amounts of $\text{CH}_2=\text{C=O}$ (<5%) and only traces of CH_4 and MeOH reveals, however, that the MeCO_2H absence is due to another channel which can only be methylmethylenebis(oxyl) oligomerization. Indeed, the occurrence of this sink reaction for methylmethylenebis(oxyl) is supported by the observation of an involatile material deposited on the inner part of the reactor and exhibiting weak IR absorption bands at 2914, 2844, 1585, 1201, 1024 and 1099 cm^{-1} and a strong absorption band at 1385 which



Scheme 2

are assignable^{14a} to an oxygenated oligomer not possessing carbonyl bonds. Furthermore, traces of compounds with *m/z* 164, 224, 284 (and 283) which differ by mass 60 (C₂H₄O₂) are also observed during GC-MS analyses of the decomposition products and can be assigned to products of a reaction of the *O*-centred diradical with methylmethylenebis(oxy).

In conclusion we would like to stress that the identified 1-hydroxyethyl acetate and 1-methoxyethyl formate give compelling evidence for the previously proposed mechanism of thermal SOZs decomposition involving the rearrangement of the ·OCHROCHRO· biradical^{5,6} and show that the rearrangement can in fact occur *via* both 1,4-H and 1,4-R-shift from carbon to oxygen. The latter product and the rearrangement of the Me group in the primary ·OCH(Me)OCH(Me)O· diradical has been observed for the first time. Our results show that the laser-induced decomposition of DMTO is more complex than conventional decomposition⁵ carried out under conditions at which wall effects are not eliminated. Our results also suggest that the reported complex mechanism can affect atmospheric chemistry, since the two isomeric esters can be formed in the gas-phase atmospheric ozonation of olefins provided that activated states for neat secondary ozonide and secondary ozonide formed in ozonation of olefins in atmospheric pressures are similar.

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