Laser-induced decompositions of 3,5-dimethyl-1,2,4-trioxolane (secondary butene-2-ozonide) in the gas phase

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UV (ArF and N_2) laser photolysis and IR laser photosensitized (SF_6) decomposition of gaseous secondary butene-2-ozonide (SBOZ) are shown to follow different reaction courses. ArF laser (193 nm) photolysis of SBOZ affords CO_2, CH_3OH, CH_3CHO, CH_4, HCOOH, $CH_2{=}C{=}O$ and C_1–C_4 hydrocarbons, while N_2 laser (337 nm) photolysis of SBOZ is a much slower process than SBOZ oligomerization occurring on the reactor walls. The multiple of the ArF laser induced photolytic products is in line with a complex reaction scheme involving initial O–O and 2,3 C–O bond splits of 1,2,4-trioxolane ring. Continuous-wave CO_2 laser photosensitized SBOZ decomposition affords CH_3CHO and CH_3COOH together with 1-hydroxylethyl acetate and 1-methoxyethyl formate, the products of rearrangement observed earlier in a pulsed CO_2 laser SF_6 photosensitized decomposition reported by us in a previous paper.

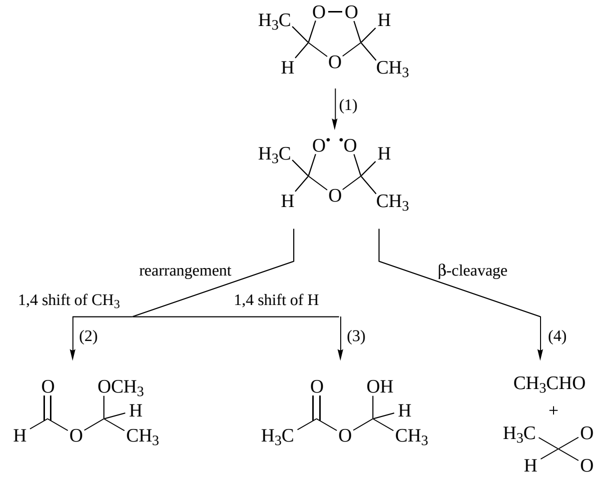
Introduction

Secondary ozonides (1,2,4-trioxolanes; SOZs) were long judged to be a part of photochemical smog, but the assessment of their role in atmospheric chemistry suffered from the lack of conclusive proof of their gas-phase formation in the ozonation of olefinic pollutants.[1] We have recently detected SOZs in the gas-phase ozonation of several alkenes providing evidence for the feasibility of their formation *via* the Criegee mechanism in the absence of a stabilizing effect of the solvent.[2]

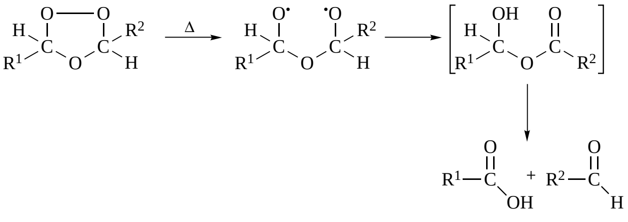
Although degradation of these oxidants in the atmosphere is naturally of great interest, studies on their gas-phase thermal and photolytical decomposition are rare. They relate to thernmal decomposition of SOZs under conditions of hot reactor surface[3] when heterogeneous contributions of the decompositions cannot be obviated, and photolysis of SOZs with 260–400 nm radiation.[4]

We have recently studied the TEA CO_2 laser-photosensitized (SF_6) (homogeneous) decomposition of 3,5-dimethyl-1,2,4-trioxolane (secondary butene-2-ozonide; SBOZ) and revealed the 1,4-H and 1,4-CH_3 rearrangement in an intermediate formed by the initial split of the O–O bond. The detected products—acetaldehyde, acetic acid, 1-hydroxyethyl acetate, 1-methoxyethyl formate and high molecular mass solid compounds—indicated that the mechanism of the homogeneous thermal decomposition is more complex (Scheme 1)[5] than previously postulated (Scheme 2).[3]

In an effort to elucidate whether the decomposition of SBOZ differs depending on the mode of excitation, we report on ArF (193 nm) and N_2 (337 nm) laser photolyses of SBOZ, as well as on homogeneous continuous-wave (CW) CO_2 laser (10.6 μm) decomposition of SBOZ in the presence of photosensitizing sulfur hexafluoride, and compare these processes to TEA CO_2 laser SF_6 photosensitized decomposition of SBOZ reported by us in the previous paper.[5]



Scheme 1



Scheme 2

Experimental

Experiments were performed by using radiation from an ArF excimer laser [Uniexport, model ELI 94, 193.3 nm, full width at half maximum (fwhm) 15 ns, repetition frequency 10 Hz], an N_2 laser (PLovdiv University, 337 nm, fwhm 10 ns, repetition frequency 10 Hz) and a grating tuned CW CO_2 laser (Institute of Chemical Process Fundamentals, 944.2 cm^{-1}, 7 W). The wavelengths, pulse energy and laser output were measured by a spectrum analyser (Optical Engineering Co.), a RJ-7620 energy ratiometer (Laser precision Corp.) and laser powermeter (Institute of Physics ASCR). The laser beam from the ArF laser was defocused by a quartz convex lens to achieve fluence of 1–3 mJ cm^{-2}.

UV laser irradiation of gaseous SBOZ was carried out in a

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Table 1 Product distribution in ArF and CO_2 laser induced decomposition of SBOZ. Products of rearrangements formed in *b* and *c* were not quantified

Laser	Pressure/kPa			Conversion (%)	Yield, mol%[a]							
	SBOZ	SF_6	N_2		CH_3CHO	CH_3CO_2H	CH_2CO	CO_2	CH_3OH	HCOOH	CH_4	C_2H_6
ArF[b]	0.11	—	100	54	10	—	5	72	60	4	13	<1
TEA CO_2[c]	0.18	0.12	8.0	45	61	13	—	—	—	—	—	—
CW CO_2[d]	0.23	0.12	8.0	73	40	16.5	<2	5	—	—	—	—

[a] As mole product per mole SBOZ decomposed. [b] 1 mJ cm^{-2}. [c] 0.7 J cm^{-2} (ref. 5). [d] 10 W cm^{-2}.

Pyrex cell of 3.6 cm internal diameter and 10 cm length fitted with pairs of NaCl and quartz windows in orthogonal configuration; the CO_2 laser irradiation of a mixture of SBOZ and sensitizing SF_6 was conducted in a similar cell fitted with a pair of NaCl windows. Both cells were furnished with a side arm having a rubber septum and a valve connecting the cell to a standard vacuum manifold.

The pressure of gases in the cells 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) as well as by gas chromatography [a GC 14 A Shimadzu gas chromatograph equipped with a flame ionization detector, a C-R5A Chromatopac data processor, columns packed with Porapak P (1.5 m), silicon elastomer SE-30 (3.3 m)]. The depletion of SBOZ was monitored at 1228 cm^{-1} and the gaseous products of the SBOZ decompositions were identified by their IR spectra and mass fragmentation. Pressures of the depleted SBOZ as well as those of the final products were calculated from the determined optical densities of authentic samples of CH_2CO, HCO_2H and C_2H_2 at 2162, 1105 and 729 cm^{-1}, respectively.

SBOZ was obtained by the ozonation of solid *trans*-but-2-ene at −125 °C and purified from oligomeric substances by trap-to-trap distillations at 0.01 kPa, the temperatures of the traps being first kept at −196 °C and ambient temperatures, and then at −196 and −50 °C. By this procedure SBOZ was obtained in purity better than 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, methanol and CO_2) of the SBOZ decompositions were from the laboratory stock.

Results and discussion

SBOZ shows a significant absorption in the emission region of an ArF laser (absorptivity at 193.3 nm *ca.* 5 atm^{-1} cm^{-1}), but rather low absorption at the region of an N_2 laser (absortivity at 337 nm *ca.* 0.1 atm^{-1} cm^{-1}).[4] We have observed that this difference in absorptivity is reflected in different photolysis rates; SBOZ (0.1 kPa) in N_2 (100 kPa) irradiated with the fluence 1 mJ cm^{-2} is efficiently depleted with the ArF laser but not at all with the N_2 laser. This is in accord with the observation that secondary ethene ozonide (1,2,4-trioxolane) does not undergo photolysis with radiation above 290 nm.[6] CW CO_2 laser photosensitized (SF_6) decomposition of SBOZ occurs due to laser energy being absorbed by sulfur hexafluoride and conveyed to SBOZ; many such thermal decompositions which occur strictly in the gas phase without contributions of heterogeneous wall effects have been reported.[7]

Laser-induced decompositions of SBOZ studied in this work give different products depending on which laser is used for the irradiation. The ArF laser photolysis of SBOZ yields carbon dioxide, methanol, acetaldehyde, methane, formic acid and ethane, while the CW CO_2 laser photosensitized (SF_6) decomposition of SBOZ gives acetaldehyde, acetic acid, 1-hydroxyethyl acetate, 1-methoxyethyl formate and traces of ketene and carbon dioxide. The same main products were also observed with the pulsed TEA CO_2 laser photosensitized (SF_6) decomposition.[5] These products are compared for high conversions in Table 1, but their formation will be discussed separately for each type of laser irradiation.

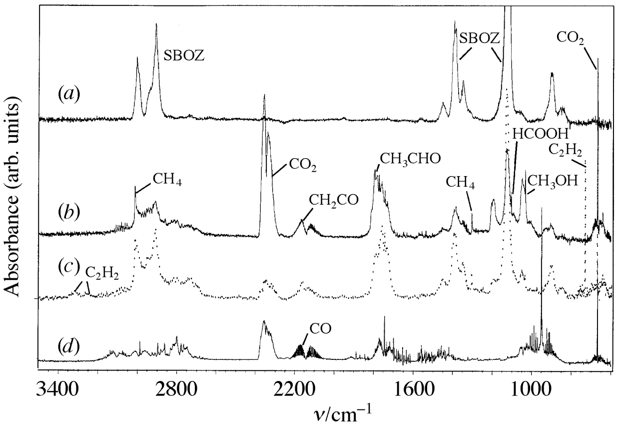


Fig. 1 Typical IR spectra of the initial (*a*) and the irradiated (*b*,*c*) SBOZ. (*a*) 0.10 kPa of SBOZ in N_2 (100 kPa). (*b*) After irradiation of SBOZ (0.10 kPa)–N_2 (100 kPa), 2.5 mJ cm^{-2}, 9600 pulses. (*c*) After irradiation of SBOZ (0.10 kPa) in N_2 (7.3 kPa), 30 mJ cm^{-2}, 250 pulses. Spectrum (*d*), added for the sake of comparison, is that of products from gas-phase reaction of ethene with O_3 in N_2.

ArF laser photolysis of SBOZ

The ArF laser irradiation of gaseous SBOZ results in the formation of a mixture of carbon dioxide, methanol, acetaldehyde, formic acid, ketene, methane, ethane, propane, butane, water and ethyne. Typical IR absorbance spectra of the SBOZ–N_2 mixture before and after laser irradiation are displayed in Fig. 1, wherein depletion of absorption bands of SBOZ at 1128 cm^{-1} is accompanied by the development of new absorption bands of CO_2 (2358 cm^{-1}), CH_3OH (1032 cm^{-1}), HCOOH (1105 cm^{-1}), CH_2CO (2162 cm^{-1}), CH_4 (1304 cm^{-1}), H_2O (1651 cm^{-1}) and C_2H_2 (729 cm^{-1}). The subtraction of spectral contributions of these compounds gives no residual spectrum and shows that no other compounds can be detected. [We note that a similar subtraction procedure applied to the mixture from the TEA CO_2 laser-photosensitized (SF_6) heating of SBOZ allowed[5] us to identify 1-hydroxyethyl acetate and 1-methoxyethyl formate as products of the SBOZ rearrangement.] The hydrocarbons, acetaldehyde and methanol were observed by GC (Fig. 2).

As illustrated in Table 2, the relative amounts of the photolysis products at *ca.* 50% conversion differ depending on the laser fluence and pressure of nitrogen. We have observed a three-fold increase in the initial rate of the photolytic depletion of SBOZ with fluence increasing from 2 to 25 mJ cm^{-2} and this indicates that the photolysis is not a biphotonic process. The major products are always carbon dioxide and methanol whose yields increase with low fluences and addition of nitrogen. The yield of formic acid is low at the high fluence in the absence of N_2, but it increases with irradiation at low fluences in the excess of N_2. The yield of ketene is almost invariant, whilst that of

Table 2 Variation of some products formed in ArF laser photolysis of SBOZ

Composition/kPa		Fluence/	Conversion	Relative yield[a] (%)				
SBOZ	N_2	mJ cm^{-2}	(%)	CO_2	CH_3OH	HCOOH	CH_2CO	C_2H_2
0.12	—	50	48	21	20	6	8	14
0.08	—	50	48	27	6	5	8	6
0.12	7.3	50	47	50	11	1	8	11
0.13	7.3	25	48	13	8	7	9	74
0.13	7.3	2	53	—	37	21	4	<3
0.07	7.3	0.6	41	50	31	11	5	0
0.12	100	1.2	45	50	43	15	7	0

[a] In absorptivity/Δ absorptivity of SBOZ.

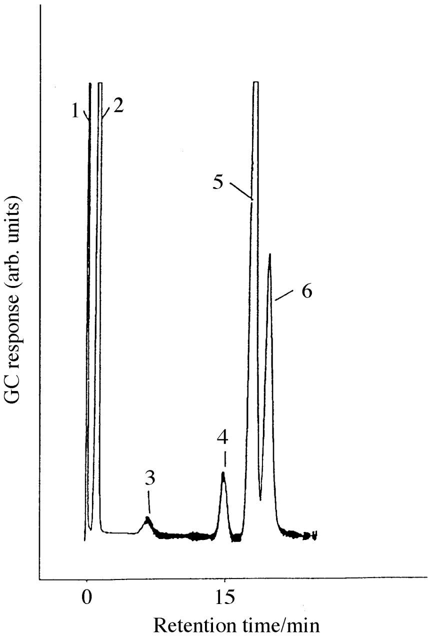


Fig. 2 Typical GC trace of the mixture from the ArF laser photolysis of SBOZ. GC conditions: Porapak P, programmed (20–80 °C) temperature. Irradiation conditions: SBOZ (0.10 kPa)–N_2 (100 kPa), 1 mJ cm^{-2}, 15 000 pulses. Peak identification: 1, methane; 2, ethane; 3, propane; 4, butane; 5, acetaldehyde; 6, methanol.

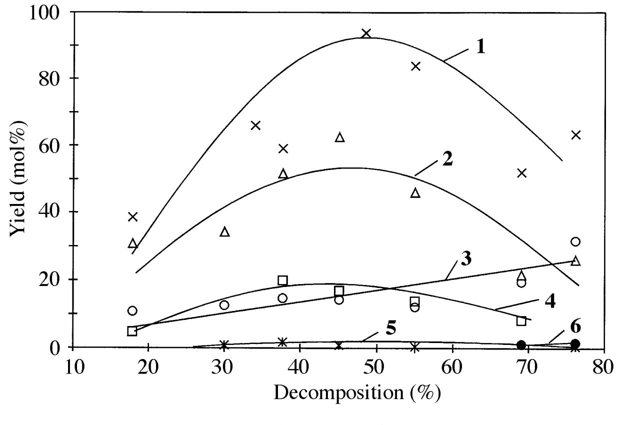
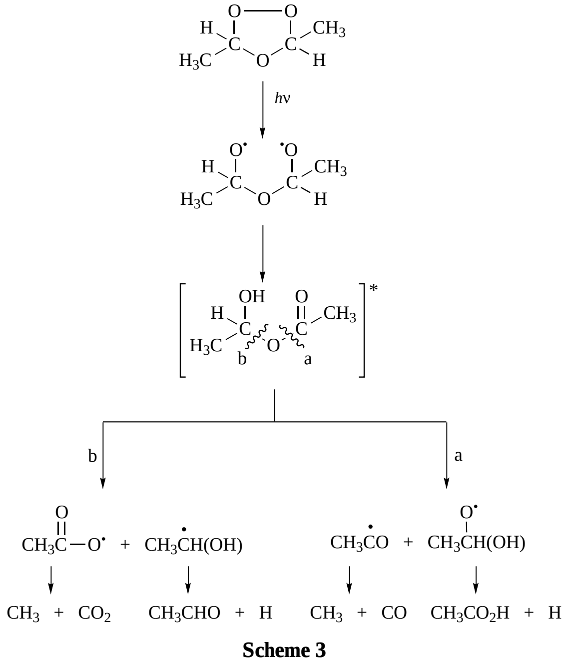


Fig. 3 Products yield as a function of conversion in ArF laser photolysis of SBOZ. Irradiation conditions: SBOZ (0.12 kPa)–N_2 (100 kPa), 1 mJ cm^{-2} (1, CO_2; 2, CH_3OH; 3, CH_4; 4, CH_3CHO; 5, C_2H_6; 6, C_3H_8).

ethyne is the most susceptible to changes in irradiation conditions. The amounts of the latter being greatest at 25 J cm^{-2} and with 7.3 kPa of N_2, and decreasing at higher fluences (in the absence of N_2), or being completely absent at the low fluences in the large excess of N_2, reveal that the formation of ethyne is affected in a complex manner. The dependence of the yields of the products on the photolysis progress (conversion) (Fig. 3) reveals that amounts of CO_2, CH_3OH and CH_3CHO increase, reach maxima at conversions *ca.* 45% and then decrease. Unlike these products, amounts of methane steadily increase over all the conversion range.

These features show that the ArF photolysis of SBOZ is a complex system of many reactions. Both acetaldehyde and methanol can be photolysed at 193.3 nm; the lamp photolysis of the former[8,9] into methane and carbon monoxide, and the latter[10] into hydrogen and formaldehyde have been reported and are likely channels. The depletion of carbon dioxide is obviously associated with formation of a complex with water.[6] The energy delivered by the photons at 193.3 nm corresponds to *ca.* 620 kJ mol^{-1}, which is much in excess of the energy needed for the cleavage of all the types of SBOZ bonds. Hence, different splits in SBOZ can occur concurrently and give rise to a myriad of consecutive reactions. We judge that plausible reactions are those included in Schemes 3 and 4.



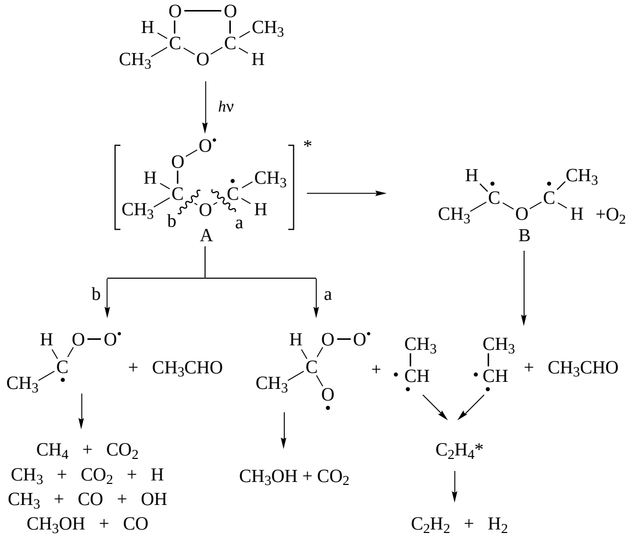
Scheme 3

Scheme 3 initiated by homolysis of the O–O bond as postulated in ref. 4 leads to the formation of the observed CO, CO_2 and CH_3CHO along with H and CH_3 species, but cannot account for the high yields of carbon dioxide and methanol, and in low N_2 pressure experiments also of ethyne and ethene. Scheme 4 beginning from the homolysis of the C–O bond (the step analogous to the C–O cleavage in peroxides by light with $\lambda < 220$ nm, ref. 11) leads to the Criegee intermediate $CH_3(H)\dot{C}{-}O{-}O^{\bullet}$. Methanol can be formed *via* an ester pathway:[12,13] $CH_3(H)\dot{C}{-}O{-}O^{\bullet} \longrightarrow [HC(O)OCH_3]^{*} \longrightarrow CH_3OH + CO$ ($\Delta H = -272$ kJ mol^{-1}) or *via* a decomposition of $^{\bullet}O{-}C(CH_3)H{-}O{-}O^{\bullet}$ into CH_3OH and CO_2. The $^{\bullet}O{-}C(CH_3)(H){-}O{-}O^{\bullet}$ species has not been assumed previously in similar photolytic decompositions, but its occurrence is justified by

Table 3 The effect of oxygen on distribution[a] of SBOZ photolytic products

Photolysed mixture[b]	Conversion (%)	CO_2	CH_3OH	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	HCOOH
SBOZ–N_2	76	64	26	32	0.33	0.6	2.9	22	10
SBOZ–air	72	100	30	15	0.07	0	0	22	35

[a] mol/mol of SBOZ decomposed. [b] SBOZ (0.15 kPa), N_2 or air (100 kPa), 2.5 mJ cm^{-2}.



Scheme 4

our thermochemical calculations based on the Benson's group additivity approach[14] and the process HO–C(CH_3)(H)–O–O–H $\longrightarrow$ $^{\bullet}$O–C(CH_3)(H)–O–O$^{\bullet}$ + 2 H$^{\bullet}$, showing that $\Delta H°_f$[$^{\bullet}$O–C(CH_3)(H)–O–O$^{\bullet}$] = −49.3 kJ mol^{-1}.

Another plausible step is an elimination of O_2 from A to give B (Scheme 4), the occurrence of which gets support from earlier mass spectral data of secondary ozonides {the observation of a fragment with *m*/*z* 72 [H(CH_3)C–O–C(CH_3)H^+] in the mass spectrum of SBOZ}[15] and from the observation of a neutral $H(CH_3)\overline{C{-}CH(CH_3){-}O}$ molecule[16] as well as possible products of its rearrangements — CH_3–C(O)CH_2CH_3 and CH_3–CH(OH)–CH=CH_2 (ref. 17) in the gas phase ozonation of *trans*-but-2-ene. The absence of a species with *m*/*z* 72 as well as of the rearranged products in our experiments is obviously related to the feasibility of photolytic decomposition of **B** into acetaldehyde and ethylidene (see also ref. 18). The observation of a preference for ethyne at the conditions (the high fluences and low pressures) which are suitable to the occurrence of highly excited species is in accord with the reported[19] ethene $\longrightarrow$ ethyne photosensitized photolysis at $\lambda = 253.7$ nm. The molecular oxygen produced and also the oxidants $CH_3C^{\bullet}(H)OO^{\bullet}$ (in Scheme 4) and $^{\bullet}OCCH_3(H)O^{\bullet}$ (in Scheme 1) can efficiently react with CH_3 radicals to yield, apart from other products, methanol.

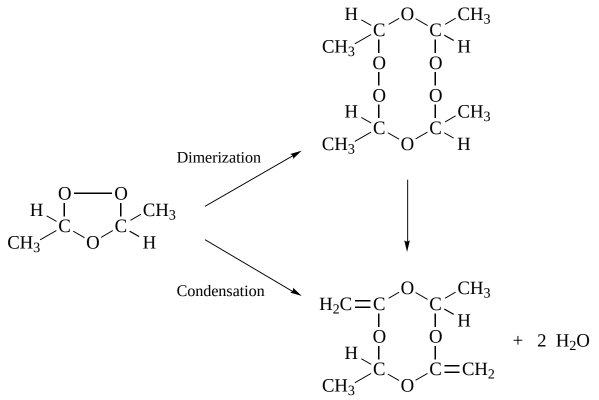
To verify the suggested effect of molecular oxygen, we have examined the ArF laser photolysis of SBOZ in the presence of air (Table 3). It is seen that the quantity of ethane, the product of the recombination of CH_3 radicals, decreased by *ca.* five times, and that of methane is twice as small. Propane and butane were not observed at all, while H_2O, CO_2 and HCOOH were obtained in larger amounts.

Molecular oxygen is a well-known quencher of triplet state species[11] and this quenching effect could result in a slower photolytic course. The irradiation of both SBOZ–N_2 and SBOZ–air mixtures for the same lengths of time resulted, however, in almost equal conversions (*ca.* 30, *ca.* 50 and *ca.* 75% with each mixture). This insensitivity of the photolytic progress but the different composition of photolytic products in the presence of air can be associated[12] with the occurrence of radical chain steps of, *e.g.*, $CH_3^{\bullet}$ and $CH_3O_2^{\bullet}$ radicals. The total picture of possible steps can be even more complex due to the fact that the 193.3 nm radiation can induce $O_2 \longrightarrow 2$ O decomposition and reactions induced by the O atoms.[11]

It is thus seen that while the data are in line with the suggested reaction schemes (Schemes 3 and 4) they are insufficient to draw more detailed conclusions on this very complex photolysis course.

N_2 laser photolysis of SBOZ

Unfocused N_2 laser irradiation (1.4 J cm^{-2}, 10 Hz) of SBOZ (0.7–0.16 kPa)—N_2 (100 kPa) did not induce formation of any volatile product. Traces of carbon dioxide, water, acetaldehyde and methanol were detected only after 5–7 h photolysis with the laser beam focused at the centre of the cell. With unfocused radiation, SBOZ was depleted by almost 30% due to formation of an involatile transparent material which deposited on the inner surface of the cell, but the same depletion of SBOZ and formation of the transparent deposit also occurred after 7 h in the dark. The FTIR spectrum of the deposited material is similar to that produced by IR laser photosensitized decomposition of SBOZ as described by us earlier.[5] The deposit can be only produced by oligomerization reactions; the simplest dimerization–condensation is depicted in Scheme 5. The former reaction would result in a ten-membered cyclic product,[20] while the latter would account for the observed increase in the absorption band of water vapour at 1651 cm^{-1} and the absorption band of the deposit at 1550–1650 cm^{-1} assignable to the ν(C=C) vibrational mode. Both dimerization and condensation are in line with the observed second-order kinetics for the dark reaction (Fig. 4), the second-order rate constant k_2 being *ca.* 1.03×10^{-21} $molecules^{-1}$ cm^3 s^{-1}. Assuming that the pre-exponential factor for bimolecular reactions A is $\leqslant 10^{-10}$ $molecule^{-1}$ cm^3 s^{-1} (ref. 13) allows us to estimate the activation energy at ambient temperature as *ca.* 63 kJ mol^{-1}, which indicates that the dimerization–condensation is a heterogeneous process.



Scheme 5

CW CO_2 laser (SF_6) photosensitized decomposition of SBOZ

The CW CO_2 laser induced homogeneous decomposition of SBOZ gives acetaldehyde, acetic acid and small amounts of ketene and carbon dioxide. These products are revealed by FTIR and GC–MS analyses (Table 1). The ratio of the two main products CH_3CHO/CH_3COOH (2.4) differs from that (*ca.*

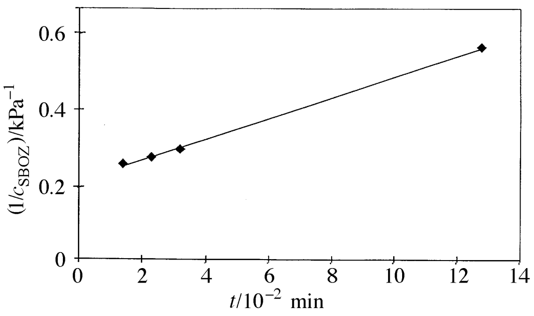


Fig. 4 Second-order decay of SBOZ (0.08 kPa) in N_2 (100 kPa) in the dark at room temperature

1.0) observed with convential thermal decomposition[3] in which hot wall effects were not obviated.

Typical IR absorbance spectra of the SBOZ–SF_6 mixture before and after laser irradiation reveal that depletion of absorption bands of SBOZ at 1128 cm^{-1} is accompanied by the development of new absorption bands of CH_3CHO (2730 cm^{-1}) and CH_3CO_2H (1292 cm^{-1}). The residual spectrum obtained by subtracting the spectral contributions of the SBOZ, CH_3CHO, SF_6 and CH_3CO_2H shows several relatively broad bands which lack rotational fine structure and are characteristic of large molecules. Their band wavenumbers can be tentatively assigned as follows: 1002, 1093, 1176 cm^{-1} (ν_{C-O}), 1274, 1369 (both ν_{C-CH_3}), 1774 cm^{-1} (ν_{CO}), 2725, 2833 cm^{-1} (both ν_{CH}) and 3590 cm^{-1} (ν_{OH}). This residual spectrum is, in fact, identical to that observed with the TEA CO_2 laser (SF_6) photosensitized decomposition of SBOZ and assigned[5] to a mixture of 1-hydroxyethyl acetate, 1-methyloxyethyl formate and diacetyl peroxide. This implies that CW CO_2 laser and TEA CO_2 laser photosensitized (SF_6) decompositions of SBOZ afford the same products and that their course can be rationalized in terms of Scheme 1. The occurrence of the three products, which were not observed in the conventional thermolysis, is apparently associated with specific conditions of the laser powered homogeneous decomposition[7a,21] which involve short heating (efficient V/RT relaxation) of molecules in a hot zone and subsequent rapid flow into colder regions. Similar cooling effect has been observed[6] in the photolysis of ethylene ozonide in which case hydroxymethyl formate was not observed in the gas phase but was trapped in the low temperature matrix.

Conclusion

The ArF laser induced decomposition of SBOZ significantly differs from the SBOZ decomposition from vibrationally excited ground state which is induced as the CW CO_2 laser photosensitized (SF_6) process.

With highly energetic photons at 193.3 nm, methanol, CO_2, CH_3CHO, formic acid, ketene and C_1–C_4 hydrocarbons are formed, while with the IR laser induced homogeneous thermal decomposition, acetaldehyde, acetic acid and 1-methoxyethyl formate and 1-hydroxyethyl acetate are produced. The products of the laser thermolysis can be explained by the reaction sequence involving the initial O–O bond split, 1,4-H and 1,4-CH_3 shifts and other steps, while those of the ArF laser photolysis can be envisaged as being formed by initial cleavage of both O–O and 2,3-C–O bonds and reactions probably involving molecular oxygen and other oxidants. N_2 laser induced photolysis of SBOZ is, obviously due to the very small absorption of 337 nm radiation, a very slow process. This photolysis takes place only with the focused radiation. With the unfocused N_2 laser radiation or in the dark, oligomerization of SBOZ is the only chemical change observed. The different chemistry in the gas phase in both UV and IR laser induced processes is also manifested by the somewhat different compositions of the deposited polymers.

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